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LATTICE ENERGY OF SALTS FORMED BY IONS WITH OUTER ENVELOPES OF EIGHT ELECTRONS

A. F. Kapustinsky and K. B. Yatsimirsky

In 1934 one of us [1], using the parallelism in the change of interionic distances and structural (Madelung) factors, proposed a simple expression for the lattice energy of ionic crystals:

$$U = 256\,\frac{\Sigma n Z_K Z_A}{r_K + r_A}, \tag{1}$$

where Σn is the number of atoms in the molecule and Z_K, Z_A, r_K, r_A are the charges and Goldschmidt radii, respectively, of the cations and anions. This equation became well known and was used by numerous investigators.

In 1943 we were successful in taking into account the quantum-mechanical character of the repulsive forces and in refining the original equation [2]:

$$U = 287.2\,\frac{\Sigma n Z_K Z_A}{r_K + r_A}\left(1 - \frac{\rho}{r_K + r_A}\right), \tag{2}$$

where $\rho = 0.345$.

This equation was used to calculate the lattice energy of not only binary compounds but also of ionic compounds with polyatomic and complex ions [3].

Later the problem arose of the accuracy and limits of applicability of the equations for the energy of the crystal lattice. S. A. Barkov's attempt [4] to solve this problem cannot be considered satisfactory, since, for calculating the experimental values of the lattice energy, this author used the heats of formation of gaseous anions, found by Bichowsky and Rossini [5] via theoretically calculated values of the lattice energy. These values in most cases were taken from Shermann's compilation [5] from which lattice-energy values were used which were calculated by Born's equation. Therefore, S. A. Barkov [4] in actuality compared lattice-energy values obtained by Equations (1) and (2) with values which cannot be considered experimental. The lattice-energy values that this author used (for certain salts: NaBr, NaI, KBr, KI and others) for comparison differ quite substantially from the experimental values.

In order to solve the problem of the accuracy and limits of applicability of Equations (1) and (2) it is necessary first of all to obtain experimental values for the lattice energy by a method that is independent of crystallochemistry. Moreover, it is necessary to evaluate the magnitude of possible error in the determination of these values, since without such evaluation, comparison of the two series of values has no meaning.

The lattice energy is understood to be the change of enthalpy during the process

$$K_m A_{n\,(\mathrm{sol})} = mK^{z_K+}_{(\mathrm{gas})} + nA^{z_A-}_{(\mathrm{gas})}.$$

Hence, the lattice energy may be calculated by equation:

$$U=m\Delta H_K^0+n\Delta H_A^0-\Delta H_{K_mA_n}^0. \quad (3)$$

In this equation ΔH_K^0, ΔH_A^0 are the heats of formation of the gaseous ions from the elements under standard conditions and $\Delta H_{K_mA_n}^0$ is the heat of formation of the crystalline salt from the elements under the same conditions. The difference in the lattice-energy values at absolute zero and under standard conditions is not great and never exceeds 0.5 kcal [7]. Therefore, in all that follows we use the lattice-energy values that relate to standard conditions. This approach is justified not only by the fact that for certain salts we lack the necessary data for conversion to absolute zero but also by the fact that interionic distances were also determined under standard conditions.

The heats of formation of gaseous cations may be determined at present with a high degree of accuracy. They represent the sum of the ionization potential (total) and the heat of sublimation of the metal. The ionization potentials are calculated from spectral data with an accuracy of up to hundredths of a kilocalorie in the case of monovalent metals and tenths of a kilocalorie in the case of divalent metals. The heats of sublimation of metals are determined with a sufficient degree of accuracy from their vapor pressures. Table 1 gives the most reliable values of the heats of formation of gaseous cations, borrowed from the latest thermochemical compilation [8] and checked against the primary sources.

The heats of formation of crystalline salts were determined also with a fully satisfactory degree of accuracy and may be checked by means of multiple "cross" comparisons. The most reliable data were obtained upon comparison of the heat of solution of the salt at infinite dilution and the sum of the heats of formation of the corresponding ions. The data on the heats of formation of crystalline salts were taken from the same compilation [8] and were also checked against the primary sources. In carrying out this verification we detected an error in the value of the heat of formation of CsF (correct $\Delta H_{298}^0 = -137.9$, given $\Delta H_{298}^0 = -135.9$). Here, the authors [8] evidently introduced an arithmetical error. The possible errors in the determination of the heats of formation of the crystalline salts that we discuss below do not exceed 0.1-0.2 kcal.

In order to calculate the heats of formation of gaseous halide anions it is necessary to know the heat of formation of gaseous atoms, calculated from spectral data (dissociation of molecules) and from vapor-pressure data at different temperatures for those elements which under normal conditions exist in a condensed state. For the heat of dissociation of F_2 we took one of the most reliable and recent values [9]. The electron affinity of the halogens and the corresponding evaluation of the possible error of determination were borrowed from Pritchard's compilation [7], in which the given values of the electronic properties were obtained by means of comparing the data found via the most diverse methods. In contrast to the data that S. A. Barkov used [4] and the data of compilation [5], these figures were obtained by a method independent of crystallochemistry. A compilation of the heats of formation of gaseous anions is given in Table 2.

Table 3 gives the lattice-energy values, calculated by Equation (3), using converted data. The possible error in the lattice-energy determination hardly ever exceeds ± 1%. The reliability of the values obtained may be judged also by comparing them with data calculated on the basis of the study of the thermal dissociation of the vapors of the discussed salts [10-15]. In almost all cases there is a very satisfactory agreement between these two series of values. An exception is the lattice energy of RbBr determined by Helmholtz and Meyer [10]. Evidently, both values for the lattice energy (RbBr and NaCl) that these authors obtained are low. A value was subsequently obtained for NaCl [12] that agreed with that found from the thermodynamic data.

The lattice-energy values found by Equations (1) and (2) are given in Table 4. The difference between these and the experimental values are given also. The lattice energy of lithium salts was not calculated, since the literature still lacks reliable data on the value for the radius of this ion.

The errors in the calculation of the lattice energy by Equation (1) are distributed within rather broad limits (from −8.5 to +4.4 kcal in the case of salts of type MX and from −22 to +32 kcal for salts of type MX_2

TABLE 1

Energy Characteristics of Certain Elements of the First and Second Main Groups of the D.I. Mendeleev System

Elements	Heats of formation of gaseous atoms (σ)	Total ionization potential	Heats of formation of gaseous cations
Li	37.07 ± 0.05	125.79 ± 0.03	162.9 ± 0.1
Na	25.98 ± 0.05	120.03 ± 0.03	146.0 ± 0.1
K	21.52 ± 0.10	101.56 ± 0.03	123.1 ± 0.1
Rb	20.51 ± 0.10	97.80 ± 0.03	118.3 ± 0.1
Cs	18.83 ± 0.20	91.25 ± 0.03	110.1 ± 0.2
Mg	35.9 ± 0.5	525.9 ± 0.5	561.8 ± 1
Ca	46.0 ± 0.5	417.5 ± 0.5	463,6 ± 1
Sr	39.2 ± 0.5	388.6 ± 0.5	427.8 ± 1
Ba	42.0 ± 0.5	353.7 ± 0.5	395.7 ± 1

TABLE 2

Energy Characteristics of Halogens

Halogens	Heats of formation of gaseous atoms ($1/2D_{X_2} + \sigma$)	Electron affinity of atoms	Heats of formation of gaseous ions
F	18.85 ± 0.2 [9]	83.5 ± 2 [7]	—64.7 ± 2.2
Cl	29.0 ± 0.1 [8, 7]	88.2 ± 1.5 [7]	—59.2 ± 1.6
Br	26.7 ± 0.1 [8, 7]	81.6 ± 1.5 [7]	—54.9 ± 1.6
I	25.5 ± 0.1 [8, 7]	74.6 ± 1.5 [7]	—49.1 ± 1.6

which amounts to from −6.3 to +4.4%). The magnitude of the error, as seen from the figure, depends on the sum of the ionic radii. When Equation (2) was used to calculate the lattice energy, the errors were included within rather narrow limits (from −4.3 to −6.6 kcal for salts of type MX and from −7 to −20 kcal for salts of type MX_2). The magnitude of the error is practically independent of the sum of the ionic radii. Equation (2) fully takes into account the effect of the interionic distance on the magnitude of the lattice energy but gives systematic negative deviations.

When Equation (2) is used to calculate the heats of formation of gaseous ions, then, in contrast to Equation (1), constant values are obtained. Equation (2) is not an empirical expression; it embodies our conceptions of the Coulomb interaction and of the quantum-mechanical nature of the repulsion of the electron envelopes of ions that form the lattice of a heteropolar crystal.

TABLE 3

Experimental Lattice-Energy Values

Salts	Lattice energy		Salts	Lattice energy, calculated from thermodynamic data
	calculated from thermodynamic energy	calculated* from thermal dissociation		
LiF	244.4 ± 2.2	—	CsBr	149.5 ± 1.8
LiCl	201.4 ± 1.6	201.3 + 3 [12]	CsI**	141.5 ± 1.8
LiBr	191.7 ± 1.6	—	MgF_2	696 ± 5
LiI	178.6 ± 1.6	177.9 ± 3 [13]	$MgCl_2$	597 ± 4
NaF	217.2 ± 2.3	—	$MgBr_2$	576 ± 4
NaCl	185.0 ± 1.7	181.3 ± 3 [10] 184.7 ± 3 [12]	MgI_2	550 ± 4
NaBr	177.1 ± 1.7	177.7 ± 3 [14]	CaF_2	624 ± 5
NaI	165.7 ± 1.7	166.7 ± 3 [15]	$CaCl_2$	535 ± 4
KF	192.7 ± 2.3	—	$CaBr_2$	515 ± 4
KCl	168.0 ± 1.7	166.4 + 3 [12]	CaI_2	493 ± 4
KBr	161.9 ± 1.7	161.2 ± 3 [14]	SrF_2	588 ± 5
KI	152.3 + 1.7	151.6 ± 3 [15] 153.6 ± 3 [11]	$SrCl_2$	507 ± 4
RbF	184.8 ± 2.3	—	$SrBr_2$	489 ± 4
RbCl	162.0 ± 1.7	—	SrI_2	465 ± 4
RbBr	156.4 ± 1.7	151.3 ± 3 [10]	BaF_2	553 ± 5
RbI	147.7 + 1.7	145.2 + 3 [13]	$BaCl_2$	483 ± 4
CsF	174.8 ± 2.4	—	$BaBr_2$	466 ± 4
CsCl	154.4 ± 1.8	—	BaI_2	441 ± 4

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*The figures used here were checked against the primary sources and corrected by Pritchard [7].

**The lattice energy, calculated from thermal dissociation, by [7], for CsI = 142.8 ± 3 [11].

The two numerical factors (287.2 and 0.345) that it contains are not arbitrary or empirically chosen proportionality coefficients. The first of them contains values of rational physical constants and also serves for "isoenergy" translation (in calculation) of any ionic lattice to a lattice of the sodium chloride type; the values of the second are derived from the compressibility of the crystals and, to a great degree, also permit calculation (total) of the van der Waals forces.

Since, during the twelve years that passed since this expression was established, there have been no significant changes (nor are they to be expected in the future in view of the fact that they are constants, determined with the highest degree of accuracy) in the magnitudes of the constants which lead to the factor 287.2, namely, in the values of the electron charge, the Avogadro number, structural coefficients, the factor for conversion of electrical units to heat units, it is unfeasible to apply corrections to this magnitude with respect to usage or refinement of the equation.

Factor 0.345 is quite a different matter. As was noted above, the basic method of finding this value is the experimental method which is comparatively unreliable; therefore, each improvement in the corresponding experimental methods will naturally be reflected in the numerical value of this factor, designated in what follows as ρ.

Among the parameters entering into our equation, the number of atoms in the molecule and the valences of the ions (Σn and Z_K and Z_A) are completely accurate, the ionic radii in the Goldschmidt system are sufficiently reliable and, therefore, during the years since their establishment (1927-1955) they were not subject to any changes and, within the limits of accuracy of one percent, successfully served to solve a number of quantitatively soluble problems. If, in the future, some changes are made in the ionic radii, these refinements will inevitably be reflected in the corresponding reevaluation of constant ρ which enters into the expression for the repulsive forces that play the chief role in the dimensions of effective ionic radii.

Wide application of the universal equation in diverse calculations demands that it be further refined. In this connection, particular attention to the value of ρ is the natural path we must follow to attain more accurate calculations. In reality, ρ is different for different crystals and the simplicity of Equation (2) necessitates our taking a somewhat averaged-out value for ρ [16]. It is therefore logical to clarify the conditions, first of all, on which ρ depends and also whether it is possible to express this dependence in Equation (2). The clarification of this problem is impossible theoretically and a semi-empirical solution is expedient.

However, the theoretical premises are quite clear. In theoretical calculations we usually consider the interaction of point charges. In passing to ion-spheres of a definite volume we depart from that model and the more so, the greater the dimensions of the ions; therefore, the correction to be introduced should not involve charges and should be directly dependent on the sum of the ionic radii. The same fact is very apparent in calculations of van der Waals potential for halides and hydrides of alkali metals.

The utilization of new data for experimental evaluations of the energy of the crystal lattice permits determination of a new value for coefficient ρ by means of Equation (2). It is not difficult to see that this value is a mean and, as it follows from the very method of its determination from experimental data, the best sample corresponding to the results of thermochemical investigations.

$$U = 287.2 \frac{\Sigma n Z_K Z_A}{r_K + r_A} \left(1 - \frac{0.30}{r_K + r_A}\right) \qquad (2a)$$

Here it is possible, however, to further refine the value of ρ which, as it follows from its very derivation, is found in a certain dependence on interionic distances.

If the sum of the ionic radii is used to evaluate the interionic distances, then this refinement of factor ρ may be expressed by the formula:

$$\rho = 0.345 - 0.00435 (r_K + r_A)^2. \qquad (4)$$

TABLE 4

Lattice Energy, Calculated from Ionic Radii

Salts	U_1 by Equation (1) (data 1934)	$\Delta_1 = U_1 - U_e$	U_2 by Equation (2) (data 1943)	$\Delta_2 = U_2 - U_e$	U_4 by Equation (5)	$\Delta_4 = U_4 - U_e$
NaF	221.5	+ 4.4	211.5	− 5.7	216.5	− 0.7
NaCl	183.4	− 1.6	180.3	− 4.7	185.3	0.3
NaBr	174.1	− 3.0	172.5	− 4.6	177.5	0.4
NaI	161.0	− 4.7	161.0	− 4.7	166.0	0.3
KF	192.4	− 0.3	187.9	− 4.8	192.9	0.2
KCl	163.0	− 5.0	162.7	− 5.3	167.7	− 0.3
KBr	155.5	− 6.4	156.3	− 5.6	161.3	− 0.6
KI	145.0	− 7.3	146.9	− 5.4	151.9	− 0.4
RbF	181.4	− 3.4	178.6	− 6.2	183.6	− 1.2
RbCl	155.1	− 6.9	155.9	− 6.1	160.9	− 1.1
RbBr	148.4	− 8.0	149.8	− 6.6	154.8	− 1.6
RbI	138.7	− 9.0	141.1	− 6.6	146.1	− 1.6
CsF	171.7	− 3.1	170.5	− 4.3	175.5	0.7
CsCl	148.0	− 6.4	149.4	− 5.0	154.4	−0.0
CsBr	141.8	− 7.7	143.9	− 5.6	148.9	− 0.6
CsI	133.0	− 8.5	135.9	− 5.6	140.9	− 0.6
MgF_2	728	32	683	−13	698	2
$MgCl_2$	593	− 4	577	−20	592	− 5
$MgBr_2$	(560)	(−16)	(550)	(−26)	565	−11
MgI_2	(515)	(−35)	(512)	(−38)	527	−23
CaF_2	643	19	617	− 7	631	7
$CaCl_2$	535	0	528	− 7	542	7
$CaBr_2$	508	− 7	506	− 9	521	6
CaI_2	471	−22	473	−20	488	− 5
SrF_2	591	3	575	−13	590	− 1
$SrCl_2$	498	− 9	497	−10	512	5
$SrBr_2$	476	−13	476	−13	491	2
SrI_2	443	−22	447	−18	462	− 3
BaF_2	556	3	546	− 7	560	7
$BaCl_2$	474	− 9	475	− 8	489	6
$BaBr_2$	453	−13	457	− 9	471	5
BaI_2	423	−18	430	−11	445	4

Upon insertion of this empirical expression in Equation (2):

$$U = 287.2\,\frac{\Sigma n Z_K Z_A}{r_K + r_A}\left[1 - \frac{0.345 - 0.00435\,(r_K + r_A)^2}{r_K + r_A}\right], \qquad (5)$$

or if put in a form that is more convenient for calculation:

$$U = 287.2\,\frac{\Sigma n Z_K Z_A}{r_K + r_A}\left[1 - \frac{0.345}{r_K + r_A} + 0.00435\,(r_K + r_A)\right]. \qquad (5a)$$

The values for the lattice energy, calculated by Equation (5), are given in Table 4. Comparison of these values with the experimental values shows that the errors are distributed statistically and the mean-square deviation for salts of type MX is 0.8 kcal (on the average about 1%).

If we agree that the error of a single calculation should not exceed twice the mean-square deviation, then the limiting errors for salts of type MX is 1.6 kcal and for salts of type MX_2 10.4 kcal. The deviations in almost all cases do not exceed the given limits with the exception of MgI_2. The possible reasons for this deviation are considered below. It must be noted that greater accuracy from the equations cannot be expected upon using ionic radii, since the values of the ionic radii are determined with an accuracy not exceeding ± 1%.

The correctness of suggested Equation (5) was verified on 30 salts which related to at least nine structural types (NaCl, CsCl, CaF_2, TiO_2 and others).

The correctness of the equation under consideration was corroborated also by the fact that in the case of salts of type MX_3 there was observed a fully satisfactory agreement between calculated values and values found by thermochemical data. Table 5 presents a similar type of comparison; in this case, all the necessary thermochemical values were taken from reference source [8]; we do not have data for evaluating the accuracy of the initial values.

TABLE 5

Lattice Energy of Salts of Type MX_3

Formula of salt	Lattice energy by Equation (5)	Lattice energy from experimental data [8]	Difference (in %)
$ScCl_3$	1165	1160	+0.4
$ScBr_3$	1126	1136	—0.5
YCl_3	1087	1074	+1.1
$LaCl_3$	1038	1014	+2.4
YI_3	975	1012	—3.7
LaI_3	936	948	—1.3

Considerably larger deviations were observed in the case of salts with sharply expressed polarization (cations with 18-electron and incomplete outer shells). In this case, the deviations may sometimes reach 10-15%. In such cases Equation (5) may be used for calculating the energy of polarization. Polarization is quite apparent even in the case of MgI_2.

We used Equation (5) for calculating the lattice energy of oxides, sulfides and selenides of metals of the first and second main groups of the D.I. Mendeleev periodic system. The data obtained are given in Table 6.

The heats of formation of gaseous anions O^{2-}, S^{2-} and Se^{2-} may be calculated from Equation (3), since all the other magnitudes are known. In almost all cases the values obtained for the heats of formation of the gaseous ions were constant. Hence, Equation (5) is also applicable for calculating the lattice energy of salts of type M_2X and $M^{II}X^{II}$. More or less considerable deviations (of the order of 17-25 kcal) were observed only in the case of salts of sodium with doubly charged anions. The reason for these systematic and approximately constant deviations remains unexplained.

If the heats of formation of the gaseous atoms O, S and Se [7] are used, then it is possible to calculate for them the magnitude of the electron affinity:

$$O_{(gas)} + 2e = O^{2-}_{(gas)} \qquad \Delta H = 172 \pm 5,$$
$$S_{(gas)} + 2e = S^{2-}_{(gas)} \qquad \Delta H = 100 \pm 2,$$
$$Se_{(gas)} + 2e = Se^{2-}_{(gas)} \qquad \Delta H = 117 \pm 2.$$

TABLE 6

Lattice Energy of Oxides, Sulfides and Selenides

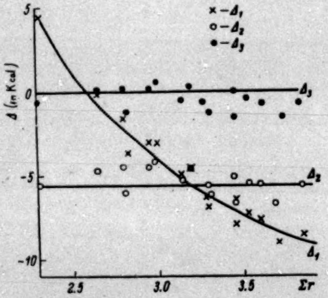
Oxides	Lattice Energy	Heat of formation of $O^{2-}_{(gas)}$	Sulfides	Lattice Energy	Heat of formation of $S^{2-}_{(gas)}$	Selenides	Lattice Energy	Heat of formation of $Se^{2-}_{(gas)}$
MgO	934	229	MgS	807	162	MgSe . . .	—	—
CaO	845	230	CaS	740	161	CaSe . . .	704	166
SrO	789	220	SrS	696	161	SrSe . . .	664	158
BaO	751	222	BaS	666	164	BaSe . . .	638	168
Na_2O	651	(260)	Na_2S . . .	567	(186)	Na_2Se . . .	539	(185)
K_2O	580	246	K_2S	512	166	K_2Se . . .	489	164
Rb_2O	552	236	Rb_2S . . .	490	170	Rb_2Se . . .	460	—
Cs_2O	527	231	Cs_2S . . .	471	169	Cs_2Se . . .	451	—
Mean value		231 ± 6			165 ± 3			165 ± 3

SUMMARY

1) Experimental lattice-energy values for halides of the first and second main groups of the D. I. Mendeleev system were calculated.

2) It was shown that: a) utilization of modern experimental data on the lattice energies of the lattices of ionic crystals permits more accurate ascertainment of the value of the repulsion coefficient (ρ = 0.30); b) increased accuracy in the ascertainment of the value of this coefficient is based on it empirically determined dependence on the sum of the ionic radii; the equation of the energy of the crystal lattice, taking this dependence into account, was shown to be valid with an error of up to 2%.

3) The lattice energy was calculated for oxides, sulfides and selenides of elements of the first two main groups of the periodic system and the electron affinity of oxygen, sulfur and selenium was also calculated.



Dependence of differences between calculated and experimental lattice-energy values (Δ_1, Δ_2, Δ_3) on sum of ionic radii (Σr). See Table 4 for interpretation of Δ_1, Δ_2 and Δ_3.

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METHODS OF ESTABLISHING THE MECHANISM OF THE CO-PRECIPITATION OF RADIOELEMENTS WITH PRECIPITATES OF DIFFICULTLY SOLUBLE SALTS

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One of the most important methods of practical radiochemistry is the carrier method, which involves the co-precipitation of the radioelement with gravimetric quantities of stable element, more or less close in properties to the radioelement being isolated. Therefore, many works, beginning with the well known investigations of K. Fajans [1] and F. Paneth [2] were devoted to the study of the laws of co-precipitation of radioelements and also of non-radioactive electrolytes present in solution in very small concentrations with precipitates of difficultly soluble salts. As V. G. Khlopin [3] and O. Khan [4] showed, different types of co-precipitation are possible which differ from each other in mechanisms and governing laws. The distinguishing characteristics of different types of co-precipitation enabled us to attain considerable success in studying the laws of co-precipitation of radioelements with precipitates of difficultly soluble salts.

It is very important to be able to experimentally determine the nature of the co-precipitation mechanism in each particular case. A number of experimental methods permitting the solution of this problem were suggested by O. Khan [4] and V. G. Khlopin [3].

However, the success that was attained in the study of co-precipitation phenomena during this time has necessitated a critical re-examination of these methods and this is the subject of the present article.

The most important types of co-precipitation of radioelements with precipitates of difficultly soluble salts may be described in the following order.

I. Co-crystallization: the radioelement distributes itself over the whole volume of the precipitate. Co-crystallization takes place only when the radioelement forms with the oppositely charged ion of the solid phase a compound that is isomorphous with the precipitate. The quantity of radioelement that passes into the precipitate during co-crystallization is determined by the distribution law of Khlopin [3].

II. Adsorption: the radioelement concentrates on the surface of the crystal-solution boundary.

1. Adsorption on polar crystals. a) Primary exchange adsorption: the adsorbate ions lose their hydration envelope and enter into the surface layer of the lattice of the precipitate. b) Secondary exchange adsorption: the adsorbate ions do not become dehydrated and become fixed in the layer of solution contiguous to the precipitate by the electrostatic attraction of the surface charge.

2. Adsorption on precipitates of salts with a molecular lattice. Although O. Khan [4] showed that adsorption on such precipitates (for example mercurous halides) is considerably less than on precipitates of polar salts, nevertheless, under favorable conditions it may reach a considerable magnitude.

The different types of co-precipitation may be differentiated experimentally by investigation of the quantity of radioelement that passes into the solid phase, depending on the following factors: 1) time (kinetics of co-precipitation), 2) amount of specific surface, 3) addition of other multivalent ions, 4) change of concentration of precipitate-ions themselves. The first two factors permit differentiation of co-crystallization from adsorption. Since during co-crystallization, the radioelement should distribute itself over the whole volume of the precipitate, establishment of equilibrium during mixing of the inactive precipitate with the solution containing the radioelement takes considerable time (2-3 weeks at room temperature). Correspondingly, the quantity of radioelement that passes into the solid phase, upon being added to a prepared suspension, is considerably less than upon precipitation of the carrier in presence of the radioelement. During adsorption, equilibrium is established rapidly (10-15 minutes) and, therefore, the magnitude of sorption depends but little on when the radioelement is added.

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*Deceased.

The effect of the amount of specific surface also differs in co-crystallization and adsorption. In the first case, the quantity of radioelement that passes into the solid phase does not depend on the quantity of crystals. During adsorption, the quantity of sorbed radioelement is directly proportional to the amount of specific surface and therefore falls when the precipitate crystals become larger due to recrystallization or change in the precipitation conditions.

Effect of multivalent ions. The study of this factor was used at times to distinguish co-crystallization from adsorption, especially by O. Khan and his school [4]. However, such a practice is faulty, since with respect to the effect of multivalent ions, the laws of co-crystallization and primary exchange adsorption are identical. Since only isomorphic ions may participate in primary exchange adsorption, the addition of non-isomorphic multivalent ions should not affect the magnitude of primary exchange adsorption. The correctness of these concepts was confirmed experimentally in the study of the adsorption of radium on lead sulfate.*

The results obtained are given in Table 1. For comparison we give the data obtained by O. Khan for the co-precipitation of Ra with potassium sulfate [4], effected via secondary exchange adsorption.

TABLE 1

Effect of Multivalent Ions on the Adsorption of Ra

Adsorbent	Added Salt	Quantity of added salt (in mg)	Percent Ra adsorption
$PbSO_4$	—	—	44.6
	$Th(NO_3)_4$	0.1	44.2
	$Th(NO_3)_4$	1.0	44.6
	$Ce(NO_3)_3$	1	47.8
	$Ce(NO_3)_3$	5	43.6
	$Sr(NO_3)_2$	1	35.4
	$Ca(NO_3)_2$	1	36.1
K_2SO_4	$Ca(NO_3)_2$	—	27.6
	$Bi(NO_3)_3$	0.001	19.9
	$Bi(NO_3)_3$	1.0	2.0

In the case of primary exchange adsorption, non-isomorphic ions, even tri- and tetravalent ions, do not show a marked effect on the magnitude of adsorption in amounts that sharply decrease the magnitude of secondary exchange adsorption. Addition of isomorphic divalent ions markedly affects the magnitude of primary adsorption. It is thus evident that the study of the effect of multivalent ions may be used to distinguish primary and secondary adsorption, but not adsorption and co-crystallization.

Dependence of magnitude of adsorption on concentration of precipitate ions themselves is different for all three types of adsorption. The dependence of the percent adsorption x on the concentration of the (precipitate) ions themselves m is expressed for different types of adsorption by the following equations: a) primary exchange adsorption**

$$\frac{x}{100 - x} m = \text{const } [5,7];$$

b) secondary exchange adsorption (for appreciable surface charge):

$$\left(\frac{x}{100-x}\right)^{\frac{1}{n_0}} = \alpha + \beta \log m \; [6, 8],$$

where α and β are constants, n_0 is the charge of the radioelement ion;

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*Carried out by R. P. Ryskina.

**An analogous expression is applicable also during cocrystallization; therefore, the study of the dependence of the concentration on the (precipitate) ions themselves on the percent adsorption as well as of the effect of multivalent ions, may serve to differentiate the types of adsorption but not to differentiate adsorption and cocrystallization.

c) adsorption on precipitates of salts with a molecular lattice: the precise form of the dependence is unknown but in practice $\underline{x}$ changes little with change in $\underline{m}$ within wide limits, as seen from Table 2 in which data are given for the adsorption of thorium C on Hg_2I_2.* Table 2 also gives data on thorium C adsorption on AgBr.**

While for 30-fold increase of the concentration of anions the thorium C adsorption on Hg_2I_2 almost does not change, upon adsorption on AgBr it increases almost two-fold upon 10-fold increase of the concentration of anions.

TABLE 2

Concentration of excess anions $\underline{m}$	Percent adsorption	
	Hg_2I_2	AgBr
$1 \cdot 10^{-3}$	52	43.9
$6 \cdot 10^{-3}$	52	80.2
$1 \cdot 10^{-2}$	—	84.7
$3 \cdot 10^{-2}$	55	—

SUMMARY

1) An analysis was made of experimental methods of studying the mechanism of co-precipitation.

2) It was shown that the study of the effect of multivalent ions permits differentiation of primary and secondary adsorption but does not permit differentiation of adsorption from co-crystallization.

3) It was shown that the study of the dependence of the magnitude of adsorption on the concentration of the (precipitate) ions themselves permits differentiation of the adsorption types.

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*Obtained by A. P. Lebedev.

**Obtained by E. N. Romanova.

STUDY OF PROPERTIES OF ACID SULFATES OF POTASSIUM

N. S. Bannykh and Ya. E. Vilnyansky

Kendall and Landon [1] studied system K_2SO_4-H_2SO_4 in the range of temperatures from -35 to 300°. In the region of high potassium sulfate concentrations they established the existence of two Compounds X and Y with a transition point from the first to the second at 238°; however, they failed to establish the composition of these compounds.

In order to arrive at the possible composition of these solid phases we investigated compounds of potassium sulfate with sulfuric acid, in which the content of the latter was less than 50 mole %. Of all the known and described hydrosulfates of this type the most probable was tripotassium hydrobisulfate $K_3H(SO_4)_2$, the presence of which in the form of the solid phase in system $K_2SO_4 - H_2SO_4 - H_2O$ was established by a number of authors [2-4] at temperatures from 0 to 75°; therefore, we studied certain properties of this acid sulfate that were not described in preceding works.

In obtaining tripotassium hydrobisulfate, we made use of solubility data on system $K_2SO_4 - H_2SO_4 - H_2O$ [4]. The salt was crystallized from a solution containing 34.4% K_2SO_4, 15.4% H_2SO_4 and 50.2% H_2O by cooling from 80° to room temperature. The crystals were separated off in the form of platelets of almost rectilinear hexagonal form (Figure 1), which fluoresced weakly at the time of formation. The main bulk of crystals ranged 0.1-0.15 mm in size. The largest crystals ranged 0.5-0.6 mm. After separation from the mother liquor, washing with ether and drying in air, analysis of crystals revealed 16.0% H_2SO_4 (15.8% by formula). Upon standing in air for a week, the weight of the crystals was unchanged. This leads us to believe the crystals of tripotassium hydrobisulfate are not hygroscopic.

A strong double refraction was found in the crystals upon investigation in polarized light. The refractive indices were determined by the immersion method with a Becke series: N_p 1.474 and N_g 1.527, magnitude of double refraction $\Delta = N_g - N_p = 0.053$. The crystals were biaxial, negative sign. The extinction was oblique and the angle of extinction with N_g for three measurements was 38°.

To determine the melting point of $K_3H(SO_4)_2$ we used a thermographic method. The salt was in an open glass test tube which was placed in an electric furnace. The temperature of the salt was measured by a thermocouple of noble metals by means of an "Etalon" potentiometer. The mean total error of the thermocouple and potentiometer readings was ± 3°.

The heating curves show two temperature halts: the first, more prolonged, in the temperature range of 207-213° and a second, less prolonged, at 270°. The first temperature halt was characterized by loss of transparency and absence of marked changes in the crystal form and was explained by us as a polymorphic transformation of the tripotassium hydrobisulfate. Only the second halt corresponded to incongruent melting of the salt. On the basis of the thermoanalytical data, the incongruent melting point of tripotassium hydrobisulfate was found by us to be 268 ± 3° with a transition from one modification to the other in the temperature range 207-213°.

Visual observations during the melting of the tripotassium hydrobisulfate crystals and microscopic analysis of the cooled melt succeeded in establishing that the melting of the salt takes place according to the scheme of the peritectic reaction: $K_3H(SO_4)_2 \rightleftharpoons K_2SO_{4\,\text{sol.}}$ + solution, with the formation of crystalline potassium sulfate and a liquid phase which may be considered as a saturated solution of potassium sulfate in fused potassium bisulfate. This solution undergoes change with rise of temperature. Starting from 350° it decomposes with evolution of water vapor in the gaseous phase.

In order to determine the composition of Compounds X and Y in system $K_2SO_4 - H_2SO_4$, we checked the separate points of the respective polytherms of these compounds; for this we used an optical method of investigation. A microfurnace was constructed, similar to the furnace used to investigate crystallization in transparent melts [5], connected with the objective of a microscope. The preparation of the salt and anhydrous acid were prepared in accordance with the tabulated data [1]. A sample of the preparation on a glass plate was put inside the furnace, the temperature of which corresponded to or was somewhat higher than the saturation temperature of the preparation. After the preparation converted to the liquid state, upon slow cooling of the melt, the formation of the solid phase was observed under the microscope.

Optical analysis of the first three preparations, from which, according to the data of Kendall and Landon, two should contain Compound X and the third – Compound Y, showed that in all three cases, upon cooling the melts, tripotassium hydrobisulfate crystallized. In the following fourth and fifth samples bipyrimidal crystals, which were similar to those that formed upon fusion of tripotassium hydrobisulfate and corresponding to potassium sulfate in optical properties, separated out as the solid phase (see table).

Solubility in Binary System Potassium Sulfate – Sulfuric Acid at High Temperatures

Temperature	Composition of saturated solution by data[1] (in %)		Solid phase	
	H_2SO_4	K_2SO_4	by data of Kendall and Landon	by our observations
220°	32.78	67.22	X	$K_3H(SO_4)_2$
236	31.69	68.31	X	$K_3H(SO_4)_2$
264	30.91	69.09	Y	$K_3H(SO_4)_2$
297	30.15	69.85	Y	K_2SO_4
300	28.56	71.44	Y	K_2SO_4

These observations permitted us to conclude that the polytherms of the saturated solutions, corresponding to Compounds X and Y, belong to tripotassium hydrobisulfate and potassium sulfate and the transition point from the first compound to the second corresponds to temperature 268°. This value exceeds the value obtained for Compound X by Kendall and Landon by 30°. The reason for this disagreement, in our opinion, lies in the method of determining the solubility. The polythermal visual method used by these authors in the region of high potassium-sulfate concentration, as we established, is of little use; therefore, the transition point 238° that they determined in this manner from Compound X to Compound Y cannot be considered reliable.

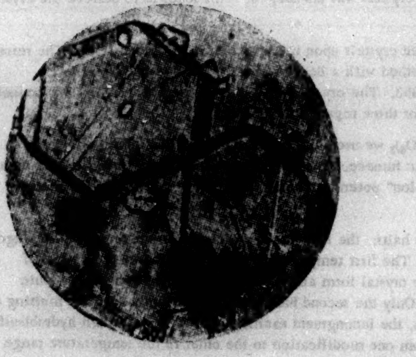

Fig. 1. Crystals of tripotassium hydrobisulfate (X 190).

The results of the present investigation together with the data on potassium bisulfate [2,6] permit addition to and correction of the solubility diagram which we studied previously to some extent in system potassium sulfate – sulfuric acid. The added elements of the diagram are given in Figure 2 by heavier lines. The melting point and points of polymorphic transformations of potassium bisulfate were taken from the data of work [6].

The diagram is of significance in the establishment of the temperature regime for preparing potassium sulfate from potassium chloride and sulfuric acid.

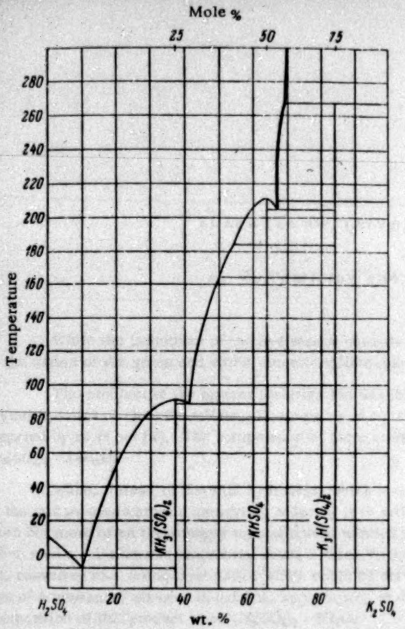

Fig. 2. Solubility diagram in binary system potassium sulfate – sulfuric acid.

SUMMARY

1) On the basis of an investigation of the properties of tripotassium hydrobisulfate, we established its presence at temperatures below 268° in binary system potassium sulfate – sulfuric acid.

2) We determined the incongruent melting point of tripotassium hydrobisulfate (268 ± 3°) and the transition point from one modification to the other (210 ± 3°).

3) We established that the melting of tripotassium hydrobisulfate takes place by a peritectic reaction scheme with formation of crystalline potassium sulfate and a liquid phase which is a saturated solution of potassium sulfate in fused potassium bisulfate.

4) The previously studied solubility diagram of binary system potassium sulfate – sulfuric acid was supplemented to some extent.

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SULFATES OF TRIVALENT CHROMIUM

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While the isomerism of the hydrates of chromic chloride has been studied quite thoroughly, the problem of the nature of the green and violet chromic sulfates has as yet been insufficiently investigated.

The problem of the present investigation was the obtaining of certain data relative to the nature of the crystal hydrates of chromic sulfate. The crystals of chromic sulfate are usually colored violet. This form was prepared by us as per [1]. The composition of these crystal hydrates corresponds in analytical data to the formula $Cr_2(SO_4)_3 \cdot 18H_2O$.

When, instead of chromic hydroxide, which is usually used as the starting material for the preparation of the salt, we used chromic anhydride, reducing it in sulfuric acid solution, a fine grey-green precipitate came down but more often the strongly supersaturated solution did not yield a precipitate even after long standing. When such a solution was evaporated down, a thick viscous dark-green mass formed which, upon drying in the air, converted to a resinous substance which could be drawn out in fine threads. Further drying led to the formation of a substance, vitreous in external appearance, readily soluble in water. The analytical data show the composition of this product to be $Cr_2(SO_4)_3 \cdot 8H_2O$.

EXPERIMENTAL

The viscosity of solutions of violet chromic sulfate (Figure 1, Curve I) increases only slightly with increase of concentration. In saturated solution (1.27 M) it was only 7.7 centipoises.

The curve of viscosity change of solutions of green chromic sulfate as a function of concentration in a part of its interval almost coincides with the same curve for solutions of the violet modification; but starting from concentration 1.27 M the viscosity of green sulfate solutions sharply increases, and at a concentration of 1.84 M equals 289.9 centipoises (Figure 1, Curve II).

The thermographic investigation of both forms of chromic sulfate that we carried out indicates that in the green modification the water is held more firmly.

In actuality, two endothermal and one exothermal effect were noted on the thermogram of the green chromic sulfate (Figure 2) that we obtained by the method of differential thermal analysis, using an N. S. Kurnakov pyrometer. The first took place at 120-125° and corresponds to the removal of 2.6 moles of water; the second, also an endothermal effect, took place at 440-445° and corresponds to the removal of the remaining water. At about 650° chromic sulfate converts exothermally to chromic oxide.

The thermogram of the violet sulfate (Figure 3) shows two endothermal effects; the first at 80-85° corresponds to the melting of the substance and loss of 10 molecules of water, and the second at 110-115° corresponds to removal of the remaining water.

The mean molecular weight, determined cryoscopically in a centimolar solution, proved considerably greater in the case of the green sulfate than for the violet (table). Taking into account the high conductivity of the solutions of both forms of chromic sulfate, i.e. the rather thorough dissociation process, it must be admitted that in solutions of both modifications there are particles with a very large molecular weight (the given data are mean values, but in the solution anions $SO_4^{=}$ with a relatively small formula weight are definitely present). Thus, it must be assumed that in solutions of chromic sulfates there takes place the formation of

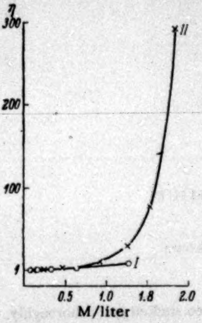

Fig. 1. Viscosity of solutions of violet (I) and green (II) chromic sulfates as function of concentration.

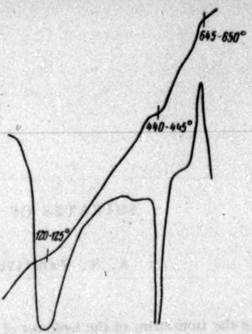

Fig. 2. Thermogram of green chromic sulfate.

complexes with high molecular weights. This process involving formation of certain large particles is very marked (judging from the values of the mean molecular weights) in solutions of the green modifications. Certain authors [2-4] explain the greater molecular weight in green solutions by the presence of polymerization. The data that we obtained on the viscosity of green solutions coupled with the relationship of the mean molecular weight values we just discussed really give us definite grounds to suppose the presence of polymerization in green solutions (a high viscosity value often is really due to the presence of polymerization). However, these results are not sufficient for categorical assertions that polymerization is present, but they indicate the direction to be followed in order to achieve a definitive solution of this problem.

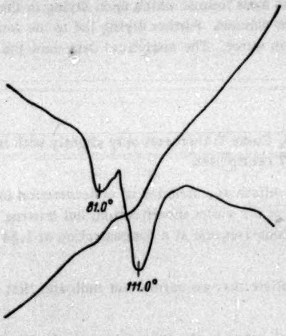

Fig. 3. Thermogram of violet chromic sulfate.

Heating of the violet solution to 60-65° brings about transition of the color to green; however, the mean molecular weight of this solution is appreciably less than the mean molecular weight found upon investigation of the solution obtained by dissolving the solid green chromic sulfate, which indicates, probably, the difficulty with which equilibrium is established in green solutions.

The change of the violet color to green is accompanied by a slight decrease in the hydrogen-ion concentration. Thus, for example, in a millimolar solution it falls from $5 \cdot 10^{-4}$ to $4 \cdot 10^{-4}$. The change in color is therefore not associated with the formation of basic salts as certain authors suppose [5]. Increase of the degree of hydrolysis becomes appreciable only above 70°. Heating the solution to 80° brings about increase in the hydrogen-ion concentration to $13 \cdot 10^{-4}$.

Mean Molecular Weight of Chromic Sulfates in Centimolar Solutions

Preparation	Color	Mean molecular weight
$Cr_2(SO_4)_3 \cdot 18H_2O$	Violet	261
$Cr_2(SO_4)_3 \cdot 8H_2O$	Green	405
Solution of violet sulfate after heating to 80° and changing to green	–	303

SUMMARY

1) The preliminary investigations of viscosity and mean molecular weight that were carried out on solutions of the green and violet modifications of chromic sulfate give definite grounds for seeking the reason for the difference in both of these forms in polymerization phenomena that take place in solutions of the green modification.

2) A slight decrease in the hydrogen-ion concentration with change in color from violet to green indicates that this change is not due to the process of hydrolysis.

3) Water is held more firmly by the green modification of the chromic sulfate hydrate than by the violet modification.

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PREPARATION OF FUSED TANTALUM CARBIDE

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The melting of very refractory substances is usually carried out in electric furnaces that operate by the resistance or electric arc method. In the investigation of tantalum carbide, one of the most refractory compounds known to science (m.p. 4150° K), there arose the problem of not only melting the material but also of effecting this process with the maximum speed in order to avoid, as much as possible, thermal dissociation of the carbide, to carry out the fusion under conditions precluding contamination of the melt with the material of the apparatus and the gases contained in it, to investigate after fusion the change of composition and lattice spacing of the carbide in order to characterize the actual extent of the carbide decomposition (observed at high temperatures in earlier investigations), to find the simplest possible route of obtaining fused, very refractory, hard bodies in the form of pieces, drops, etc.

EXPERIMENTAL

For this purpose we assembled a small furnace based on the electric arc principle. The circuit diagram of the assembly and melting apparatus is shown in Figure 1.

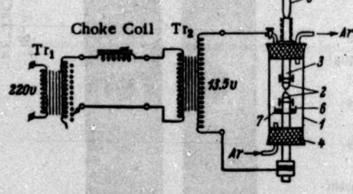

Fig. 1. Circuit diagram of assembly and scheme of apparatus for preparing fused tantalum carbide. 1) Quartz tube, 2) electrodes, 3) copper holders, 4) rubber stoppers, 5) handle for moving electrode, 6) small tantalum cup, 7) tantalum carbide powder.

The furnace is a cylindrical quartz tube, diameter 60 mm, length 400-500 mm into which two copper rods, equipped on the ends with copper clamps (electrode holders), enter through rubber stoppers (covered inside with asbestos). In place of rubber stoppers, copper sections may be ground to fit the ground ends of the quartz tube. The electrode material consisted of rectangular pressed bars of tantalum carbide, composition "$TaC_{0.90}$",* having a face-centered cubic structure (γ-phase) [1], sintered in the quartz furnace that was previously described [2]. The special feature of the apparatus was the detachable upper electrode. Melting was carried out in an atmosphere of spectroscopically pure argon. After establishing the current via the choke circuit and filling the apparatus with argon, we carefully screwed in the upper electrode until formation of an arc. The voltage on the furnace terminals was 13.5 V.

After the arc had burned for several seconds, the circuit was broken and the furnace was cooled in an atmosphere of argon. On top of the lower pressed bar (electrode) of "$TaC_{0.90}$" we detected a drop of fused carbide, diameter 5-6 mm. The formation of drops was corroborated by photographs (Figure 2).

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*In the case of preparations, not single-phase, used in our laboratory, our custom is to write the true composition of the phase without quotation marks. The gross composition of a preparation, not single-phase, is written in quotation marks.

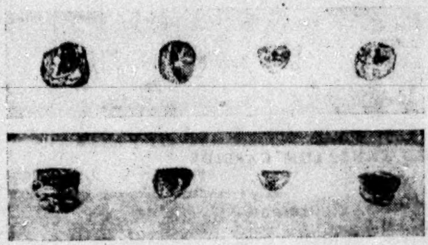

Fig. 2. Melted drops of tantalum carbide(1:1).

Fig. 3. X-ray photographs of initial (a) and fused (b) tantalum carbide.
a) "$TaC_{0.90}$" b) "$TaC_{0.85}$" c) graphite (002).

To carry out the fusions in large quantities the apparatus was modified so that the lower electrode was fitted with a collector-cylinder of sheet tantalum with an opening in the bottom corresponding to the cross section of the pressed bar. The bottom of the cylinder was covered with powder of the same composition as the pressed bar (Figure 1). Such an assembly permits the fusion to be carried out for a longer period of time, since the drops of fused tantalum carbide that form fall into the collector-cylinder which precludes damage to the apparatus by carbide (heated to 4150° K) and contamination of the latter due to reaction with other materials. Figure 1 shows cup 6 fitted on holder 3. Usually we place it on lower electrode 2.

The x-ray photograph, taken of the fused preparation, differs from the x-ray photograph of the initial preparation by the presence of a relatively sharp graphite (002) line (Figure 3). The lattice spacing, determined by the asymmetrical method, was equal to 4.450_8 A (before fusion), which corresponds to a composition of carbide phase $TaC_{0.86}$ [1] and 4.444_5 A (after fusion) which corresponds to a composition of carbide phase $TaC_{0.80}$. These results agree well with the data of chemical analysis. It is evident from these data that the rapid fusion of TaC_x in an electric arc in an argon atmosphere is associated with a slight carbon loss. It is known from the literature [3] that when TaC is heated to lower temperatures in atmosphere of hydrogen and nitrogen, a considerably stronger decomposition occurs. According to the data of [3], the fusion product was a mixture of tantalum carbide and 30-65% metallic tantalum. Due to the accumulation of the latter on the surface of the pressing even at 3000° K, there occurred surface fusion and the metal flowed down along the carbide stick; therefore, it was to be feared that at temperatures above 4000° K decomposition of the carbide would reach a very appreciable extent. In actuality, it is possible to effect fusion under the above described conditions very rapidly and with relatively slight change in composition, i.e. obtain fused carbide in the simple apparatus. The x-ray photograph of our product shows only the presence of the γ-phase line (cubic) of tantalum carbide and one graphite line. The lines of metallic Ta are absent on the x-ray photograph. The above-described simple method of fusing refractory hard materials of the TaC type permit the use of a similar compact apparatus for solving diverse theoretical problems associated with the investigations of similar materials.

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RECIPROCAL EFFECT OF HYDROXIDES DURING FRACTIONAL PRECIPITATION FROM THEIR SOLUTION

N. N. Mironov and A. I. Odnosevtsev

The separation of elements on the basis of the different solubility of their hydroxides, known as basic fractional precipitation, has been studied for a long time by investigators, especially in relation to the rare-earth elements.

A detailed survey of the methods of separating rare-earth elements was carried out in the review article of D. I. Ryabchikov and E. A. Terentyeva [1]. The theoretical problems of precipitation received detailed treatment in the works of N. A. Tananaev and associates [2]. Some of the laws they derived relate to the conditions of precipitating metal hydroxides.

These problems were further developed in the works of I. M. Korenman [3,4] which relate to the study of the dependence of hydroxide precipitation on the pH of the medium.

However, up to now the problem of the reciprocal effect of hydroxides during precipitation from a solution containing a mixture of salts has not been clarified. In all cases of separation it is assumed that the hydroxides will behave the same in mixture as they behave separately in solution, i.e. that their precipitation goes in sequence with change in pH of the solution. However, it is certain that there is a reciprocal hydroxide effect. The present work is devoted to a study of certain laws that govern this reciprocal effect.

We investigated with following systems:

$Ti(OH)_4$ + $Fe(OH)_3$,
$Ti(OH)_4$ + $Al(OH)_3$,
$Ti(OH)_4$ + $Ce(OH)_3$,
$Ti(OH)_4$ + $La(OH)_3$,
$Fe(OH)_3$ + $Al(OH)_3$.
$Fe(OH)_3$ + $Ce(OH)_3$,
$Fe(OH)_3$ + $La(OH)_3$,
$Al(OH)_3$ + $Ce(OH)_3$,
$Al(OH)_3$ + $La(OH)_3$.

For the experiments we used nitrates of analytical grade which we recrystallized. The exception was titanium, the nitric acid solution of which was prepared by solution of the freshly-precipitated hydroxide in nitric acid. The titanium content in the solution was then determined gravimetrically. The salt concentrations in the solutions were 0.02 N.

In our investigation we used the method of potentiometric titration. Ammonia, which was obtained by means of bubbling air through an aqueous solution of ammonia, was used as the titrating reagent. The ammonia method we selected has certain advantages over other known methods. First of all, by passage of air through solutions containing low concentrations of ammonia it was possible to obtain a very low ammonia content in the titrating gaseous mixture and, hence, secure a smooth pH change of the medium. The course of the titration curve agrees exactly with many points. Secondly, the phenomenon of a sharp local pH change, which always is obtained at the delivery point of the precipitatant (even if very dilute), can be avoided to a great degree. This is quite essential in working with salt mixtures. Finally, upon using the given method, dilution of the solution does not occur which is important when small concentrations are precipitated from solution.

The diagram of the apparatus on which the investigation was carried out is shown in the illustration. The wash bottles with caustic soda solution are for the purification of air from carbon dioxide. The flow rate

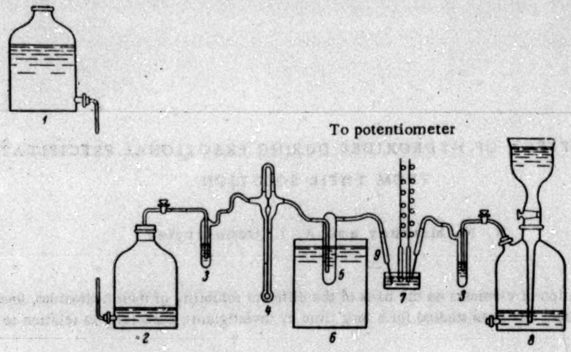

Diagram of apparatus.

1) Delivery bottle, 2) bottle for compressed air, 3) wash bottles with caustic soda solution, 4) flowmeter, 5) bottle with ammonia solution of known concentration, 6) thermostat, 7) titration vessel, 8) gasometer, 9) capillary for delivery of gaseous mixture into the solution.

of the gaseous mixture was 0.3 ml/ sec., which was accomplished by selecting a suitable capillary for the flowmeter. The temperature of the aqueous ammonia solution was held at 20° by means of the thermostat.

To secure steady operation of lead capillary 9, air pressure was created in vessel 2 by means of elevated bottle 1. For more thorough mixing, additional air was delivered from the gasometer in the vessel with the titrated solution.

Measurement of the pH of the medium was taken by means of a glass electrode and a lamp-galvanometer ("MOSKIP" type LP-5). The accuracy of the pH readings was within ± 0.05 pH units. The pH reading was taken after 60 and 30 seconds. The adjusting of the potentiometer was carried out before work was started on a buffer mixture KCl - HCl with pH 2.00.

With the same regime we carried out 3-4 experiments, from the results of which we plotted on one graph the curves of the dependence of pH on the quantity of ammoniacal mixture and then a resultant curve which was taken as the mean for the calculations. A comparison of the tangents of the slope angles of the curves established the point where the curvature of the plot changed. The pH value at this point was taken as the pH corresponding to the start of hydroxide precipitation.

The results of the pH measurements at the start of hydroxide precipitation are given in Table 1.

As we see, the pH at the start of hydroxide precipitation rises when another salt, capable of giving a difficultly soluble hydroxide, is present in solution.

It would be correct to explain this rise in pH at the start of precipitation of hydroxides by increase in the ionic strength of the solution. However, as a rule, the ionic strength of the solution, in passing from experiment to experiment, changed negligibly and, due to this, in the given case it is necessary to assume a more complex reaction mechanism. The following facts indicate this. Visual observation of the coming down of the precipitate from solution shows that from a mixture of salts the precipitate comes down with more difficulty and retardation in comparison to a solution of only one salt.

We tried to establish the pH at the start of coagulation: upon appearance of a persistent turbidity in the solution, i.e. at the start of apparent coagulation, the pH of the solution was noted. The results are given in Table 2.

TABLE 1

pH at Start of Precipitation of Hydroxides from Salt Mixtures

Ions	pH at start of precipitation	Ionic strength of solution	Ions	pH at start of precipitation	Ionic strength of solutions
$Ti^{\cdot\cdot\cdot\cdot}$	1.40	0.172	$Fe^{\cdot\cdot\cdot} + Al^{\cdot\cdot\cdot}$	2.60	0.194
$Ti^{\cdot\cdot\cdot\cdot} + Fe^{\cdot\cdot\cdot}$	1.55	0.212	$Fe^{\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	2.80	0.186
$Ti^{\cdot\cdot\cdot\cdot} + Al^{\cdot\cdot\cdot}$	1.50	0.220	$Fe^{\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	2.70	0.172
$Ti^{\cdot\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	1.45	0.184	$Al^{\cdot\cdot\cdot}$	3.55	0.100
$Ti^{\cdot\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	1.45	0.208	$Al^{\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	3.70	0.135
$Fe^{\cdot\cdot\cdot}$	2.45	0.152	$Al^{\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	3.80	0.132

TABLE 2

pH at Start of Coagulation of Hydroxides

Ions	pH at start of coagulation	Ions	pH at start of coagulation
$Ti^{\cdot\cdot\cdot\cdot}$	1.65	$Fe^{\cdot\cdot\cdot} + Al^{\cdot\cdot\cdot}$	5.55
$Ti^{\cdot\cdot\cdot\cdot} + Fe^{\cdot\cdot\cdot}$	2.15	$Fe^{\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	5.50
$Ti^{\cdot\cdot\cdot\cdot} + Al^{\cdot\cdot\cdot}$	2.10	$Fe^{\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	5.45
$Ti^{\cdot\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	2.05	$Al^{\cdot\cdot\cdot}$	5.25
$Ti^{\cdot\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	2.05	$Al^{\cdot\cdot\cdot} + Ce^{\cdot\cdot\cdot}$	8.90
$Fe^{\cdot\cdot\cdot}$	2.55	$Al^{\cdot\cdot\cdot} + La^{\cdot\cdot\cdot}$	9.05

From a comparison of the data of Tables 1 and 2 it is evident that there is some interval of pH values between the start of the formation of hydroxide and the beginning of the settling-out of the precipitate. For certain systems this interval takes in two, three or more pH units. It is natural to suppose that, during the period of such a retarded settling-out of the precipitate, the hydroxide exists in the colloidal state. To confirm this supposition we prepared a hydrosol of iron by passage of gaseous ammonia into 0.1 N $Fe(NO_3)_3$ + $Al(NO_3)_3$ solution.

The color of the solution was an intense red, pH 4.25. The prepared solution was subjected to dialysis for 2 hours with a change of water after every 20 minutes. After dialysis, the solution was subjected to electrophoresis, as a result of which we determined the electrokinetic potential (ζ) which proved equal to 28.8 mV. Hence, the hydrosol was already quite close to the isoelectric point.

We then prepared a hydrosol of iron with pH 2.15 of the same composition as the preceding. The electrokinetic potential (ζ) of this solution was equal to 69.7 mV. This means that at pH 2.15 the solution is completely stable.

This experiment may be considered as corroboration of the fact that there is an interval of pH values, within the limits of which there exists a stable colloidal solution of ferric hydroxide. $Fe(NO_3)_3$ and also $Al(NO_3)_3$ are stabilizers, which is confirmed by the fact that aluminum was detected in the colloidal solution after dialysis of the latter. Evidently the aluminum ions enter into the composition of the colloidal particles (adsorption layer). Stabilization of the iron hydrosol is also possible via an excess quantity of $Fe(NO_3)_3$ if the colloidal solution is prepared from a more concentrated $Fe(NO_3)_3$ solution. However, it is necessary to note that the colloidal solution, stabilized by aluminum ions, is more stable.

In the same way we prepared a colloidal solution of aluminum hydroxide, stabilized by cerium ions with pH 6.05. This solution was subjected to dialysis for 4 hours. Due to the colorlessness of the solution, we could not determine its electrokinetic potential. It was shown that addition of NH_4OH causes coagulation and that the precipitate contained aluminum and cerium ions.

We made many attempts to free the colloidal solution of $Ti(OH)_4$, prepared at pH 1.72 and stabilized by $Fe^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$ ions, of electrolytes. However, upon dialysis the solution always coagulated, which indicated its considerable instability. It may be noted also that the solution, stabilized by aluminum ions, broke up more rapidly on dialysis than the one that was stabilized with ferric ions.

From the above it may be concluded that colloid-formation is evidently one of the factors that enters into the phenomenon of co-precipitation during the basic fractional precipitation of hydroxides. For the characterization of the quantitative side of co-precipitation, we carried out chemical analysis of certain binary systems gravimetrically. The precipitate to be analyzed was taken at that pH value at which the first component should be already completely precipitated. If at this pH value the precipitate was unformed (colloidal solution), coagulation was effected by heating the solution. Table 3 gives the composition of the precipitate in percent of the calculated quantity with respect to the initial weighed sample (the mean results from two determinations).

TABLE 3

Dependence of Percentage Composition on pH

System	pH at which precipitate was taken off	Yield of components (in % of weighed sample)
$Ti(NO_3)_4 + Ce(NO_3)_3$	3.85	$TiO_2 = 99.5$, $CeO_2 = 3.5$
$Ti(NO_3)_4 + La(NO_3)_3$	3.55	$TiO_2 = 99.6$, $La_2O_3 = 5.3$
$Fe(NO_3)_3 + Ce(NO_3)_3$ . . .	3.45	$Fe_2O_3 = 99.8$, $CeO_2 = 5.5$
$Fe(NO_3)_3 + La(NO_3)_3$ . . .	3.30	$Fe_2O_3 = 99.7$, $La_2O_3 = 4.1$
$Al(NO_3)_3 + Ce(NO_3)_3$ . . .	5.55	$Al_2O_3 = 99.5$, $CeO_2 = 15.5$
$Al(NO_3)_3 + La(NO_3)_3$ . . .	5.80	$Al_2O_3 = 99.8$, $La_2O_3 = 21.2$

The data of Table 3 show that the percentage of co-precipitated second component increases with increase of the pH value at which the precipitate was taken off.

Precipitation of the first component is practically complete. When the precipitation was carried out at pH values above the cited pH values, precipitation occurred of the second component alone in quite pure form.

The question arises: does capture of the ions of the second component occur during coagulation of the colloidal solution or during formation of the colloidal particles?

To determine the answer to this problem we prepared two 0.1 N $Fe(NO_3)_3$ solutions. In the first of them a colloidal solution of $Fe(OH)_3$ was formed by careful passage of gaseous ammonia. The final value of the pH of the solution was brought to 3.65 and then a known quantity of $Ce(NO_3)_3$ was added. A weighed sample of $Ce(NO_3)_3$ was also added to the second solution and a colloidal solution was also created with a final pH value of 3.75. In this experiment the colloidal solution was formed in presence of cerium ions since in the first experiment the cerium salt was introduced into an already prepared colloidal solution. Both solutions were then subjected to coagulation via heating and the composition of the precipitates was analyzed. The results obtained are given in Table 4.

TABLE 4

Effect of Colloid Formation on Composition of Precipitate

Solution No.	Coagulation pH	Composition of precipitate (in %)	
		Fe_2O_3	CeO_2
1	3.65	99.8	Traces
2	3.75	97.3	2.7

The data of Table 4 show that, evidently, the capture of cerium ions takes place during the formation of the colloidal solution when the cerium ions that are present at the moment of formation of the colloidal particles participate in the formation of these particles.

SUMMARY

1. An investigation was made of the mutual interaction of the two hydroxides during basic fractional precipitation by means of ammonia.

2. It is established that colloids are formed, and this impedes the separation process.

3. It is shown that the hydroxide which is the stronger base causes a stabilizing effect with respect to the colloid solution of the hydroxide which is the weaker base. This is evidenced especially clearly for iron and aluminum ions.

4. Colloid formation is one of the causes of the coprecipitation of the more basic hydroxide with the less basic hydroxide.

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*T.p. - C. B. Translation pagination.

REACTION OF RHENIUM WITH CYANIDES OF IRON

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Tougarinoff [1], upon investigation of the reduction products of perrhenates with stannous chloride and potassium ferrocyanide, observed the formation of a reddish product. The reaction which he discovered is used for the qualitative detection of rhenium. The author believed that heptavalent rhenium is reduced by stannous chloride to trivalent rhenium. This supposition does not agree with the works of other authors, since it is known that $ReCl_3$ gives a blue coloration with potassium ferrocyanide [2].

Tribilat [3] established the pentavalency of rhenium in the given complex compound via potentiometric analysis. These data practically exhaust the information available on this reaction; therefore, we studied the composition and properties of this complex in more detail. The study was by a physicochemical method (Ostromyslensky-Job-Babko) and a method involving ion-exchange chromatography.

EXPERIMENTAL

The solutions of potassium perrhenate were prepared by dissolving the recrystallized preparation in 5% hydrochloric acid.

The order of combining the solutions was as follows: to a solution of $KReO_4$ in a 50 ml flask was added 25 ml HCl (d 1.19), 2 ml 1% solution of $K_4[Fe(CN)_6]$ or $K_3[Fe(CN)_6]$ in water, and 2 ml 10% $SnCl_2$, dissolved in HCl (d 1.19). The remaining free space was filled up to the mark with distilled water. After each addition of the solutions, the reaction mass was stirred.

The optical density measurements were carried out after 20 minutes on a FEK-2 photocolorimeter with a blue light filter, the transmission region of which was 400-500 mμ. Upon rapid combination of the reagents, the intensity of the color does not depend upon the order in which the solutions are combined. A less intense color is obtained when solutions of $KReO_4$, HCl and $SnCl_2$ are combined and the $K_4[Fe(CN)_6]$ solution is added after several hours. This indicates that the ferrocyanide reacts only with the rhenium of valency below seven, which forms in the first moment of reduction of the perrhenate. Upon standing, the initially prepared rhenium passes over to rhenium of a lower valency with which the reaction does not go.

The change in intensity of the color as a function of the concentration of rhenium obeys the Lambert-Beer law up to a concentration of $6 \cdot 10^{-6}$ mole/liter (Fig. 1).

The molar extinction coefficient of the rhenium-ferrocyanide complex was calculated from the data used for Fig. 1 by the formula [4]: $D = \epsilon c \cdot \underline{l}$. The average value of the molar extinction coefficient is $3 \cdot 10^3$ with a blue light filter.

The colored rhenium complex is not extractable from aqueous solution with diethyl ether, ethyl acetate, butyl acetate, chloroform, carbon tetrachloride, benzene or toluene. Amyl and butyl alcohols extract the colored complex. The solvent layer turns reddish. Extraction of the colored compound with mixtures of these alcohols and chloroform on diethyl ether takes place less completely than with the pure alcohols. Upon shaking the aqueous solution of the rhenium complex with amyl and butyl alcohols, a stable emulsion forms which hinders the extraction of the small quantities of rhenium.

Ion-exchange resins, cationites of the SBS type and sulfonated coal K in the N-form did not absorb the rhenium-ferrocyanide complex. Anionite of type TM in the ON-form absorbed the complex. Upon passage of the colored solution through a column with anionite, a colorless filtrate was obtained. The upper part of the anionite layer was colored by the absorbed complex compound. The colored zone was slightly faded in the downward direction. Washing the column with hydrochloric acid solution (1:3) caused a slight displacement of the colored zone. Treatment of the column with absorbed complex by 2 N caustic soda solution caused a momentary disappearance of the colored zone, since the complex was destroyed by alkali.

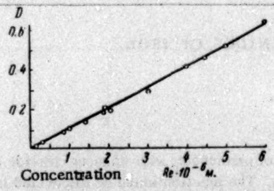

Figure 1. Dependency of color intensity on concentration of solution.

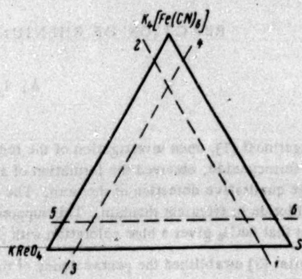

Figure 2. Diagram of cross sections.

The composition of the rhenium ferrocyanide complex was investigated by measuring the optical density of the solution along different cross sections of the triangular diagram of composition $KReO_4$ – $K_4[Fe(CN)_6]$ – $SnCl_2$ (Fig. 2).

The ratio of $[KReO_4]:K_4[Fe(CN)_6]$ in the complex was determined by studying the optical density of a series of solutions along the cross section 3-4 in Fig. 3. The initial concentrations of the solutions of potassium perrhenate and potassium ferrocyanide were equimolar and were $8.58 \cdot 10^{-4}$ M. The solutions were mixed in such a manner that the sum of their volumes was constant and amounted to 10 ml; the total concentration was $1.72 \cdot 10^{-4}$ M. The concentrations of HCl and stannous chloride were 4 and 0.40 M respectively. The volume of the solutions was 50 ml. The change in optical density of the solutions along this cross section is shown on Fig. 3. The optical density maximum was observed at the ratio $[KReO_4]:K_4[Fe(CN)_6] = 1:1$.

The change in optical density of the solutions at constant concentration of $6.8 \cdot 10^{-4}$ M for potassium perrhenate and a variable concentration of potassium ferrocyanide is given in Fig. 4. The inflexion of the curve that characterizes the dependence of the optical density on the ratio of the concentrations of these substances is not sharp. The molar extinction coefficient, according to the data of Fig. 4, is less than that calculated by the data of Fig. 1. These facts indicate dissociation of the rhenium-ferrocyanide complex. The intersection of the extensions of separate branches of this curve corroborate the above-found ratio of $[KReO_4]:K_4[Fe(CN)_6] = 1:1$.

Study of the optical density of solutions along the cross section 5-6 (Fig. 2) permits determination of the ratio $[KReO_4]:[SnCl_2]$, which enables us to ascertain the valency of rhenium in the complex under investigation. The initial concentrations of potassium perrhenate and stannous chloride were equal and were $3.07 \cdot 10^{-3}$ M. The sum of their volumes was 5 ml; the total concentration of perrhenate and stannous chloride was $3.07 \cdot 10^{-4}$ M.

A solution of stannous chloride was prepared by dissolving a weighed sample of granulated tin in concentrated hydrochloric acid in a hydrogen atmosphere. Copper compounds hinder colorimetric determination; therefore, they must not be added as is sometimes done to accelerate solution of tin. The other solutions used were saturated with sulfur dioxide and allowed to stand for a long period in this atmosphere. Preliminary experiments showed that sulfur dioxide does not exhibit reducing properties with respect to compounds of heptavalent rhenium.

The results of the investigation of the optical density of the solution along the cross section 5-6 show that the optical-density maximum was observed at the ratio $[KReO_4]:[SnCl_2] = 1:1$ (see the table).

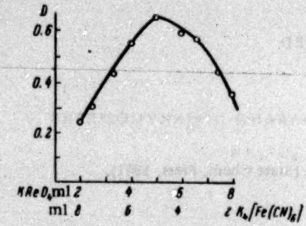

Fig. 3. Optical density of solutions along cross section 3-4.

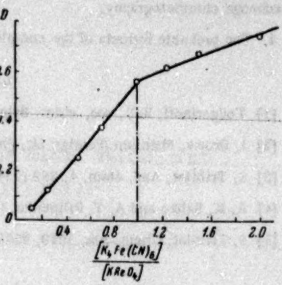

Fig. 4. Dependency of optical density of the solutions on ratio $K_4[FE(CN)_6]:[KReO_4]$.

TABLE

Optical Density of Solutions Along Cross Section 5-6 (Fig. 2)

Concentration (mole/liter) · 10^4		Ratio	Optical density
$KReO_4$	$SnCl_2$	$[KReO_4]:[SnCl_2]$	
2.05	1.02	2 : 1	0.51
1.68	1.39	1 : 0.8	0.68
1.53	1.53	1 : 1	0.71
1.38	1.69	1 : 1.2	0.62
1.23	1.84	2 : 3	0.60
1.02	2.05	1 : 2	0.54

On the basis of this, the reduction of potassium perrhenates with solutions of stannous chloride in acid medium may be expressed by the equation:

$$ReO_4^- + Sn^{2+} + 4H^+ = ReO_2^+ + Sn^{4+} + + 2H_2O.$$

Hence, the complex compound contains pentavalent rhenium. The above-cited fact of the dependence of the color intensity of the solutions on the order of combining the solutions agrees with these data. Decrease in the color intensity upon non-simultaneous combination of the solutions of potassium ferrocyanide and stannous chloride is associated with slow transition of pentavalent rhenium to tetravalent rhenium [5]. The results of our determination of the valency of rhenium by a photometric method agree with the data of potentiometric titration [3].

The behavior of the rhenium ferrocyanide complex on ion-exchange resins characterizes the colored portion of the complex as an anion.

Substitution of a 2% potassium cyanide solution for the potassium ferrocyanide solution did not secure the formation of a complex analogous to the rhenium-ferrocyanide complex; therefore, the formula $H_3[ReO_2(CN_4)]$ is excluded as a possible formula.

On the basis of the foregoing, we consider the investigated complex to have the formula $H_3[ReO_2(CN)_6Fe]$.

SUMMARY

1. It has been shown that the rhenium-ferrocyanide complex contains pentavalent rhenium.

2. A relationship has been found between the constituent parts of the complex and the magnitude of the molar extinction.

3. The anionic character of the colored portion of the complex has been proved by a method employing ion-exchange chromatography.

4. The probable formula of the complex is suggested.

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THERMODYNAMIC CHARACTERIZATION OF NaOH, Na_2CO_3 AND NA_2SO_4 AT HIGH TEMPERATURES

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For the thermodynamic characterization of NaOH, Na_2CO_3 and Na_2SO_4 we have data on the values of functions $H^0_T - H^0_0$, $Z^0_T - Z^0_0$ and $S^0_T - S^0_0$ only for standard temperature (T = 298.16° K), based on heat-capacity measurements of these substances at low temperature [1-3].

For thermodynamic analysis of the chemical reactions taking place at high temperature with the participation of NaOH, Na_2CO_3 and Na_2SO_4 in the solid or molten state, we need data on $H^0_T - H^0_{298.16}$, $Z^0_T - Z^0_{298.16}$ and $S^0_T - S^0_{298.16}$ over an extended temperature range.

We calculated these values for the temperature range 500-1500°K. For this we used equations $c_p = f(t)$ for NaOH (composition: NaOH 98.79%, Na_2CO_3 1.2%, impurities 0.01%), Na_2CO_3 and Na_2SO_4 (chemically pure), prepared previously [4].

All relationships $c_p = f(t)$, given in [4], were converted to $C_p = \varphi(T)$ by equation:*

$$C_p = a + bt + ct^2 = a + b\,(T - 273.16) + c\,(T - 273.16)^2.$$

The equations for solid and molten NaOH, containing 100% of basic substance, were formulated with allowance for the additivity of the heat capacity of caustic soda and soda for negligible contents of the latter in the product (up to 1.2%).

The difference of enthalpies $H^0_T - H^0_{298.16}$ for each of these substances was calculated by equation:

$$H^0_T - H^0_{298.16} = \int\limits_{298.16}^{T_{I\to II}} C_p dT + \Delta H_{I\to II} + \int\limits_{T_{I\to II}}^{T_m} C_p dT + \Delta H_m + \int\limits_{T_m}^{1500} C_{p(1)} dT,$$

in which $\int$ is the change in enthalpy of the substances in the given temperature range; $T_{I \to II}$, T_m are the transformation temperatures of the solid phase and the melting point respectively; $\Delta H^{**}_{I \to II}$, ΔH_m, are the respective heats of the phase transformations.

The difference of entropies $S^0_T - S^0_{298.16}$ was calculated by equation:

$$S^0_T - S^0_{298.16} = \int\limits_{298.16}^{T_{I\to II}} C_p d\ln T + \frac{\Delta H_{I\to II}}{T_{I\to II}} + \int\limits_{T_{I\to II}}^{T_m} C_p d\ln T + \frac{\Delta H_m}{T_m} + \int\limits_{T_m}^{1500} C_{p(1)} d\ln T.$$

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* Letter t denotes degrees Celsius (centigrade), T denotes degrees Kelvin.

** For Na_2CO_3 the phase transformations in the solid phase are referred to two temperatures: the first T = 593.16°K and the second T = 723.16°K.

TABLE 1

Initial Data for Calculation of $H^0_T - H^0_{298.16}$, $Z^0_T - Z^0_{298.16}$ and $S^0_T - S^0_{298.16}$

Substance	$S^0_{298.16}$ (e.u.)	$C_p = \varphi(T)$ (cal/g·deg	Temperature range (°K)	Heat effect of phase transformation ΔH° (cal/mole)
NaOH	15.3	$12.228 + 0.7995 \cdot 10^{-2} T$	298.16—576.8	Transformation* $\Delta H^0_{576.8} =$ $= 1929.7$
		$23.997 - 0.54644 \cdot 10^{-2} T$	595.16—1500	Melting $\Delta H^0_{595.16} =$ $= 1629.3$
Na_2CO_3	32.5	$14.48 + 3.902 . 10^{-2} T$	298.16—723.16	Transformation I $\Delta H^0_{593.16} = 255.01$ Transformation II $\Delta H^0_{723.16} = 448.5$
		$32.197 + 8.43 \cdot 10^{-3} T$	723.16—1123.16	Melting $\Delta H^0_{1123.16} =$ $= 7303$
		$-312.63 + 0.561574 T - 2.1949 \cdot 10^{-4} T^2$	1123.16—1500	
Na_2SO_4	35.7	$13.94 + 0.0554 T$	298.16—518.46	Transformation $\Delta H^0_{518.46} =$ $= 2068$
		$31.75 + 1.548 \cdot 10^{-2} T$	518.46—1157.2	Melting $\Delta H^0_{1157.2} =$ $= 5770$
		$136.09 - 0.072334 T$	1157.2—1500	

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* The difference of enthalpies in temperature range 576.8-595.16°K is included in the heat of fusion $\Delta H^0_{595.16}$

TABLE 2

Calculated Values of the Difference of Enthalpies $H^0_T - H^0_{298.16}$, the Difference of Isobaric Potentials $Z^0_T - Z^0_{298.16}$ and the Difference of Entropies $S^0_T - S^0_{298.16}$ of NaOH, Na_2CO_3 and Na_2SO_4 at High Temperatures (p = 1 atm.)

Substance	Temperature (°K)								
	500	700	900	1000	1100	1200	1300	1400	1500
					$H^0_T - H^0_{298.16}$ (cal/mole)				
NaOH	3112	10084	14009	15890	17716	19487	21205	22866	24475
Na_2CO_3	6066	13644	22181	26202	30307	41909	46529	50976	55060
Na_2SO_4	5882	17815	26470	31114	35914	46681	51260	55120	58255
					$Z^0_T - Z^0_{298.16}$ (cal/mole)				
NaOH	— 3946	— 9840	—17357	—21448	—25737	—30179	—34878	—39492	—44328
Na_2CO_3	— 8174	—19044	—32425	—39788	—47552	—56125	—65292	—74938	—86135
Na_2SO_4	—10519	—21913	—37622	—46172	—55203	—64883	—75259	—85954	—96911
					$S^0_T - S^0_{298.16}$ (cal/mole °C)				
NaOH	7.94	19.68	24.62	26.60	28.35	29.89	31.35	32.50	33.61
Na_2CO_3	15.36	28.04	38.94	43.18	47.09	57.27	60.97	64.36	68.09
Na_2SO_4	18.39	36.26	47.34	52.23	56.81	66.14	69.81	72.67	74.84

The difference of the isobaric potentials was calculated by equation:

$$Z_T^0 - Z_{298.16}^0 = (H_T^0 - H_{298.16}^0) - T\left(S_T^0 - S_{298.16}^0\right) - S_{298.16}^0\,(T - 298.16).$$

The initial data for the calculation of $H_T^0 - H_{298.16}^0$, $Z_T^0 - Z_{298.16}^0$ and $S_T^0 - S_{298.16}^0$ are given in Table 1; the calculated values of these functions, in Table 2.

The thermodynamic parameters at the melting point are given below.

$$\text{NaOH} \quad T = 595.16^\circ\,\text{K}$$

$$\begin{array}{lll} \text{NaOH}_{\text{sol}}\ \ H_T^0 - H_{298.16}^0 = 6311 & Z_T^0 - Z_{298.16}^0 = -5351 & S_T^0 - S_{298.16}^0 = 13.64 \\ \text{NaOH}_{\text{liq}}\ \ H_T^0 - H_{298.16}^0 = 7940 & & S_T^0 - S_{298.16}^0 = 16.38 \end{array}$$

$$\text{Na}_2\text{CO}_3 \quad T = 1123.16^\circ\,\text{K}$$

$$\begin{array}{lll} \text{Na}_2\text{CO}_{3\,\text{sol}}\ \ H_T^0 - H_{298.16}^0 = 31269 & Z_T^0 - Z_{298.16}^0 = -49397 & S_T^0 - S_{298.16}^0 = 47.95 \\ \text{Na}_2\text{CO}_{3\,\text{liq}}\ \ H_T^0 - H_{298.16}^0 = 38572 & & S_T^0 - S_{298.16}^0 = 54.45 \end{array}$$

$$\text{Na}_2\text{SO}_4 \quad T = 1157.16^\circ\,\text{K}$$

$$\begin{array}{lll} \text{Na}_2\text{SO}_{4\,\text{sol}}\ \ H_T^0 - H_{298.16}^0 = 38728 & Z_T^0 - Z_{298.16}^0 = -60560 & S_T^0 - S_{298.16}^0 = 59.30 \\ \text{Na}_2\text{SO}_{4\,\text{liq}}\ \ H_T^0 - H_{298.16}^0 = 44498 & & S_T^0 - S_{298.16}^0 = 64.29 \end{array}$$

SUMMARY

The values of the thermodynamic functions were calculated: the difference of enthalpies $H_T^0 - H_{298.16}^0$, the differences of isobaric potentials $Z_T^0 - Z_{298.16}^0$ and the difference of entropies $S_T^0 - S_{298.16}^0$ of NaOH, Na_2CO_3 and Na_2SO_4 for T = 500, 700, 900, 1000, 1100, 1200, 1300, 1400, 1500°K and for melting points (595.16°K for NaOH, 1123.16°K for Na_2CO_3 and 1157.16°K for Na_2SO_4).

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SPEÇIFIC HEAT OF Na_2CO_3, Na_2SO_4 AND NaOH AT HIGH TEMPERATURES

M. M. Popov and D. M. Ginzburg*

Thermodynamic and thermotechnical calculations of processes in which soda, sodium sulfate and caustic soda participate at high temperatures (up to 1100° and higher) has been hindered up to the present by the absence of data on the temperature dependence of the specific heat of these substances and also by the absence of data on their heats of fusion and polymorphic transformations. Determination of the values of the cited quantities is therefore the problem of the present work. The most suitable method would be that of direct heating, for example, in the form which one of us employed [1]. However, due to the fact that this method has as yet only been used in only the interval 100-700° of the high-temperature region, we had to use the classical "drop" method which we carried out by means of a massive calorimeter similar to the one described in works [2, 3]. Since the experiments were carried out under diathermal conditions, the mean specific heat was calculated by equation:

$$\bar{c}_{p\vartheta_n}^{\vartheta'} = \frac{W(\vartheta_n - \vartheta_0) - w(\vartheta' - \vartheta_n)}{P(\vartheta' - \vartheta_n)}, \tag{1}$$

where $\bar{c}_{p\theta n}^{\theta'}$ is the mean specific heat at constant pressure, W is the heat value of the calorimeter, θ_n is the final temperature of the main block, corrected for heat exchange, θ_0 is the initial temperature of the main block, $\underline{w}$ is the heat value of the ampoule in which the investigated substance was heated and in which it was introduced into the calorimeter, θ' is the constant temperature up to which the investigated body, situated in the ampoule outside the calorimeter, was heated, P is the weight of the investigated substance.

The true specific heat was calculated from the experimentally found mean via equation:

$$c_{p\vartheta} = \frac{dQ}{d\vartheta} = \frac{d\left[\bar{c}_{p\vartheta_n}^{\vartheta'}(\vartheta' - \vartheta_n)\right]}{d\vartheta}. \tag{2}$$

Since the specific heat of all three investigated substances was determined within a relatively extended temperature interval (from 20 to 1100°), it was necessary to use calorimeters of different mass(3.1 and 9 kg) and thereby raise its temperature ($\theta_n - \theta_0$) and also increase the correction for heat exchange, calculated by the Regnault-Pfaundler equation, introduced to attain a completely definite accuracy (a nominal error of ≤ 0.3%) in the determination of the mean specific heat.

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* A. V. Bilevich participated in the experimental section of the work.

EXPERIMENTAL

The construction of the calorimeter and the method of working with it are described in detail in [1, 2] and, hence, we only note certain features here.

The temperature of the calorimeter was measured by a platinum resistance thermometer (small calorimeter – wire diameter 0.05 mm, R = 30.17391Ω, large calorimeter – wire diameter 0.05 mm, R = 29.52518Ω), wound on the outer surface of the calorimeter block and is expressed in relative units – readings of the thermometric bridge. This necessitated calibration of the calorimeter, i.e. of determining its heat value W by an electric current of a known strength. This calibration was carried out for many temperature differences $\theta_n - \theta_0$ and the constancy of W was shown within the range of variation of this difference. The final temperature of the main block θ_n was expressed in degrees, for which purpose the platinum resistance thermometer was calibrated with a mercury calorimetric thermometer checked near these temperatures. This calibration was carried out by measurement of the thermometer resistance at temperature equilibrium between the calorimeter and the thermostat, which was maintained for 3-4 hours; the temperature equilibrium was attained both after positive as well as negative temperature fluctuation of the calorimeter and in both cases the results of calibration were identical. This calibration was carried out several times during the work, which permitted evaluation of the accuracy of the platinum resistance thermometer.

The investigated substances were heated and introduced into the calorimeter in ampoules. Platinum ampoules were used for sodium carbonate and sodium sulfate, and for caustic soda we used ampoules of a nichrome type alloy. The necks of the nichrome ampoules were welded to conical stoppers from the same material. The quality of the weld was determined by the weight constancy of the ampoule with caustic soda, independent of the length of time it stayed in the air and also by its constancy of weight upon heating in the furnace of the calorimetric apparatus.

The substances, placed in ampoules, were heated in the furnace with a platinum heater. Vertical equalization of the temperature in the furnace was attained up to 800° by a silver tube that was inserted in it and

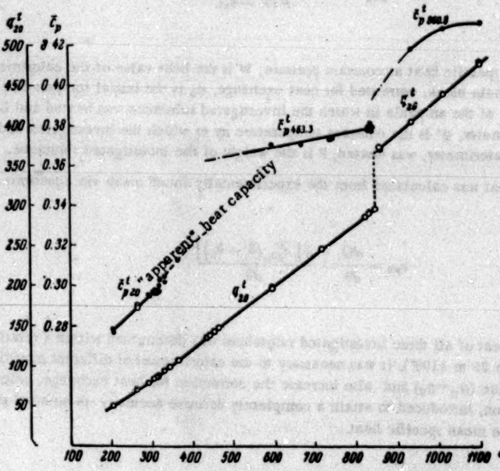

Fig. 1. Dependence of specific enthalpy and mean specific heat of Na_2CO_3 on temperature.

higher – by a stainless-steel tube. The constancy of the furnace temperature (±0.1° even at 1000-1100°) was attained by means of a photoelectric-type temperature controller.

The temperature of the ampoule was measured by a standard thermocouple Pt-Pt, Rh (10%), the junction of which was in direct contact with the ampoule. The electromotive force was determined with an "Etalon". potentiometer. A mirror galvanometer with a scale sensitivity of $0.175 \cdot 10^{-6}$ V/mm served as the null instrument.

The heat losses that occur during the fall of the ampoule, filled with substance, were excluded by the fact that during determination of the "apparent" heat capacity of the material of the ampoule (i.e. empty of substance), the latter fell into the calorimeter at the same speed as the ampoule with the substance.

The results of the "apparent" heat-capacity determinations of the material of the platinum ampoules were expressed by two equations: one for the temperature range 20-433° and the second for the temperature range 433-998.6°. These equations served to determine the heat value of the empty platinum ampoule at any experimental temperature with Na_2SO_4 as well as with Na_2CO_3.

The "apparent" heat capacity was determined for the nichrome ampoule at temperatures that exactly corresponded to the experimental temperatures in the heat-capacity determinations of caustic soda. This was because the main component of the ampoule material, nickel (80%), undergoes a polymorphic transformation near 300°.

Sodium carbonate. The sodium carbonate was chemically pure. The curve of the change in heat content of Na_2CO_3 (Figure 1) was obtained on the basis of 63 calorimetric experiments, including 20 temperature points.

On the enthalpy curve of Na_2CO_3, i.e. $q = f(t)$ we see a considerable change in $\underline{q}$ in the interval 840-860°, which corresponds to the fusion of sodium carbonate and also a bend in the curve in the interval 440-460°, which indicates a phase transformation, already noted in the literature [4]. Finally, on curve $\bar{c}^t_{P_{20}}$ we note a break in the curve at 320°, which corresponds to another phase transformation. These two phase transformations were noted by measurement of the true heat capacity of Na_2CO_3 in intervals 290-365 and 367-500° with maxima at 350 and 477° [1].*

Curve $\bar{c}^t_{P_{20}} = f(t)$ may be broken into six sections.

The first section includes the interval (202.8-20) to (318.9-20°) and is expressed by equations:

mean specific heat

$$\bar{c}^t_{P_{20}} = 0.2445 + 1.841 \cdot 10^{-4} (t - 20); \tag{3}$$

mean molar heat capacity

$$\bar{C}^t_{P_{20}} = 25.92 + 1.951 \cdot 10^{-2} (t - 20); \tag{4}$$

true molar heat capacity

$$C_p = 25.14 + 3.902 \cdot 10^{-2} t. \tag{5}$$

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* The work was carried out concurrently with the present investigation and by a method of direct heating; $\bar{c}_p = f(t)$ was determined for sodium carbonate and sodium sulfate in the temperature range 100-600°.

The fourth section includes the interval 839.1-463.3° and is expressed by equations:

mean specific heat

$$\bar{c}^{t}_{p_{463.3}} = 0.3623 + 3.976 \cdot 10^{-5}\,(t - 463.3); \tag{6}$$

mean molar heat capacity

$$\bar{C}^{t}_{p_{463.3}} = 38.405 + 4.215 \cdot 10^{-3}\,(t - 463.3); \tag{7}$$

true molar heat capacity

$$C_p = 34.500 + 8.43 \cdot 10^{-3}\,t. \tag{8}$$

The sixth section includes the temperature interval 1106.6-860.8° in which sodium carbonate exists in a molten state.

The heat capacities are expressed by the following equations:

mean specific heat

$$\bar{c}^{t}_{p_{860.8}} = 0.3956 + 3.0078 \cdot 10^{-4}\,(t - 860.8) - 0.6902 \cdot 10^{-6}\,(t - 860.8)^2, \tag{9}$$

mean molar heat capacity

$$\bar{C}^{t}_{p_{860.8}} = 41.935 + 3.1884 \cdot 10^{-2}\,(t - 860.8) - 0.73164 \cdot 10^{-4}\,(t - 860.8)^2 \tag{10}$$

true molar heat capacity

$$C_p = -175.59 + 0.441645\,t - 2.1949 \cdot 10^{-4}\,t^2. \tag{11}$$

For the 2nd, 3rd and 5th sections of curve $q^{t}_{20} = f(t)$, for which, due to transformation, it was impossible to determine the heat capacity values, there are data on enthalpy q^{t}_{20}, from which we calculated the heat effect of transformation and the heat of fusion by equation:

$$Q = (q_3 - q_1) - [\bar{c}_3\,(t_3 - t_2) + \bar{c}_1\,(t_2 - t_1)], \tag{12}$$

in which Q is the heat effect of transformation or the heat of fusion; q_3, q_1 are the enthalpies at t_3 (end of transformation) and at t_1 (start of transformation); $\bar{c}_3$, $\bar{c}_1$ are the mean heat capacities of the substance after and before transformation; and t_2 is the accepted transformation temperature.

For determination of $\bar{c}_3$ and $\bar{c}_1$ only the "normal section" of the heat capacity was considered. The product of the "anomalous" section of the heat capacity and the corresponding temperature interval was included in the heat of transformation.

Deviations of the experimental values of $\bar{c}_{p_{20}}^{t}$ from those calculated by Equation (3) amount to less than 0.1%, and with respect to Equation (6) they do not exceed ±0.3%.

For the interval 200-290° the previously found equation is [1]:

$$C_p = 25.06 + 4.184 \cdot 10^{-2}\, t, \tag{13}$$

and for interval 500-600°

$$C_p = 30.15 + 1.963 \cdot 10^{-2}\, t. \tag{14}$$

Equations (5) and (13) may be considered coincident but the non-coincidence of Equations (8) and (14) demands special consideration in connection with determination of heat effects of transformation.

Heat effect Q_1 of the first phase transformation which takes place at 320° (or in interval 290-365° [1]), calculated by Equation (12), proved equal to $Q_1 = -255.07$ cal/mole but according to work [1] $Q_1 = -200.6$ cal/mole. Heat effect Q_2 of the second transformation differs in magnitude almost by a factor of two depending on the method of determination.

On comparison of the "drop" and direct heating methods, the possible reason for the divergence may be explained thusly; in the "drop" method, when the heated sample rapidly cools in the calorimeter, quenching of the sample takes place and it is possible that it does not return to its initial state before heating. If this reasoning is correct, it should be expected that the heat effect, determined by the method of direct heating, will have an absolute value that is greater than the heat effect determined by the "drop" method.

In effect, a comparison of the enthalpy data obtained by the two methods corroborates this supposition as can be seen from the following table.

Enthalpies of Na_2CO_3 for the Temperature Region in Which Transformations Take Place
(Q is the Enthalpy of 1 Mole in the Temperature Limits Corresponding to the Indices)

No.	Temperature	Q_{20}^{t} (cal/mole in present work)	$Q_{202.9}^{t}$ (in present work)	$Q_{202.9}^{t}$ (as per data of [1])	Divergence (in %)	Note
1	202.9°	5392	—	—	—	
2	265.6	7550	2158	2186	1.25	No transformation
3	298.1	8715	3323	3395	2.2	Region of transformations
4	330.9	9998	4606	4678	2.0	
5	341.7	10442	5050	5173	2.5	
6	364.9	11408	6016	6157	2.3	
7	440.8	14620	9225	9519	3.2	
8	463.3	15548	10156	10628	4.7	
9	501.0	17004	11612	12401	—	After transformation, the divergences in Q fall to 1.5% (for example, $Q_{501}^{598.6}$ according to our data, is 3934 and according to the data of [1], it is 3996 cal/mole)
10	598.6	20938	15546	16397	5.0	

The heat capacity of sodium carbonate in the temperature interval 55-300°K was determined by Anderson [5] $c_{p_{25°}} = 26.38$ cal/mole · degree.

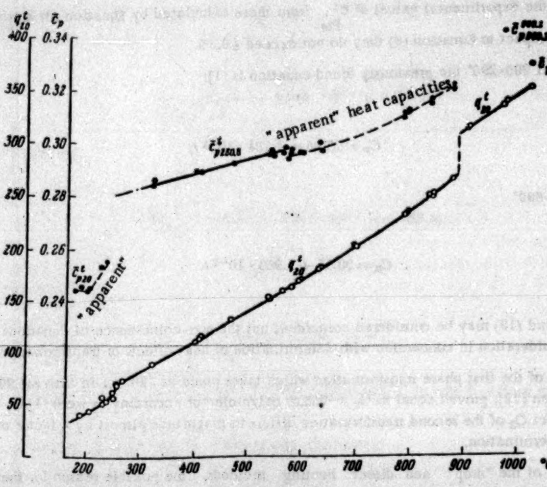

Fig. 2. Dependence of specific enthalpy and mean specific heat of Na_2SO_4 on temperature.

According to the data of the present work, the heat capacity of soda at 25° was 26.12; according to the data of [1] it was also 26.12 cal/mole · degree (extrapolation was used in both cases).

This agreement of the value of the heat capacity of soda at 25° with values obtained by other methods indicates the reliability of the "drop" method that was used for determination of heat capacity at high temperature for such substances as Na_2CO_3, Na_2SO_4 and NaOH which undergo a whole series of phase transformations upon being heated.

The heat of fusion, calculated by Equation (12), proved equal to Q = −7303 cal/mole and by the literature data of [6], the calculated value of Q, obtained as the average of a whole series of scattered experimental data on the equilibria of binary mixtures, was equal to −7000 cal/mole.

Sodium sulfate. An analytical grade of sodium sulfate was used. For investigation of Na_2SO_4 in temperature interval 20-1017.1° we carried out 65 experiments which included 22 temperature points (Figure 2).

In view of the number of transformations that take place with solid Na_2SO_4, the investigation was carried out with different ampoules and different sample weights.

In the lower region of the Na_2SO_4 investigation (197-210°), we succeeded in determining the mean heat capacity for two temperature points:

$$\bar{c}_{p_{20}}^{179.4}=0.2442, \quad \bar{c}_{p_{20}}^{188.7}=0.2446.$$

Since the temperature interval was small, it was not possible to use only our data to express the dependence $\overline{c}^t_{P_{20}} = f(t)$ by an equation. Therefore, we used the data of Pitzer [7] for the c_p of Na_2SO_4 at 300°K and for the interval 20-245.3° we found the following equations for the dependence of heat capacity on temperature:

mean molar heat capacity

$$\bar{C}^{t}_{p_m} = 30.17 + 0.0277\ (t - 20); \tag{15}$$

true molar heat capacity

$$C_p = 29.07 + 0.0554\,t. \tag{16}$$

Near 200° there is a sharp bend in the curve of mean heat capacity. In the interval from 200 to 260.8° the direction of the enthalpy curve does not obey any law and only from 260.8° does it attain a definite direction.

The literature notes that sodium sulfate undergoes five polymorphic transformations in the temperature region between 197 ± 2 and 253°, and for the polymorphic transformations associated with pronounced heat effects, different authors cite different temperatures. Thus, it was found [1] that the transformations of Na_2SO_4, accompanied with absorption of heat, take place in the interval 194.5-290.5° and that the maximum on the temperature-true heat capacity curve corresponded to 245.3°

In the temperature interval 260.8-564.4° the heat capacity is determined by the following equations:

mean specific heat

$$\bar{c}^{t}_{p_{260.8}} = 0.2818 + 5.4498 \cdot 10^{-5}\ (t - 260.8); \tag{17}$$

mean molar heat capacity

$$\bar{C}^{t}_{p_{260.8}} = 40.02 + 0.7739 \cdot 10^{-2}\ (t - 260.8); \tag{18}$$

true molar heat capacity

$$C_p = 35.98 + 1.548 \cdot 10^{-2}\,t. \tag{19}$$

In work [1] for region 290.5-600° this equation is given:

$$C_p = 36.5 + 1.600 \cdot 10^{-2}\,t. \tag{20}$$

Equations (19) and (20) may be considered to be in satisfactory agreement.

In the temperature interval 564.4-874° a sharp change takes place in the course of the heat capacity curve, which indicates the presence of still another polymorphic transformation. Near 874° the heat capacity

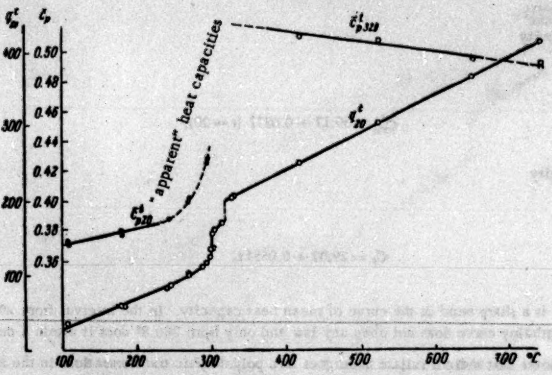

Fig. 3. Dependence of specific enthalpy and mean specific heat of NaOH on temperature.

curve sharply bends, which indicates the presence of a premelting region. Finally, the enthalpy of the fused Na_2SO_4 was determined only up to 1017.1° for three points, namely:

	q_{20}^{t} (cal/mole)
900.3 — 20°	317.38
969.2 — 20°	341.67
1017.1 — 20°	356.72

from which the heat capacities were determined:

$$\bar{c}_{p_{900.3}}^{969.2} = 0.3438 \text{ cal/g} \cdot \text{degree} \qquad \bar{c}_{p_{900.3}}^{1017.1} = 0.3316 \text{ cal/g} \cdot \text{degree}$$

From the given figures and from Figure 2 it is apparent that the heat capacity of the fused Na_2SO_4 is greater than that of the solid but it decreases with temperature. The heat effect of the phase transformation that takes place in the interval 197-260.8° and referred to 245.3°, was calculated by Equation (12).

The heat effect of the transformation proved equal to:

$$Q_1 = -2068 \text{ cal/mole.}$$

The heat of fusion, calculated by Equation (12), proved equal to: $Q_2 = -5770$ cal/mole and by the data of [6] $Q_2 = -5830$ cal/mole.

Q_1 agrees with the data in work [1] for the third heating, namely:

$$Q_1 = -2016 \text{ cal/mole.}$$

The agreement of our figure with the figure of only the third heating again indicates that the polymorphic transformations take place slowly, which hinders their thermodynamic investigation.

Caustic soda. Caustic soda was prepared by dehydration of the reagent that contained 1% Na_2CO_3 and 5% H_2O by means of its continuous fusion in vacuum at 400-425° for 1.5-2 days. The obtained preparation had the composition: NaOH 98.79%, Na_2CO_3 1.2%, impurities 0.01%.

The thermal data for NaOH were determined in the temperature interval 20-742.8° on the basis of 62 calorimetric experiments that included 16 temperature points (Figure 3).

For the experiments we used ampoules with the following sample weights of caustic soda: 5.8974, 4.8200 and 4.0790 g.

The control for the constancy of the contents of the welded ampoules was the similarity of the results obtained while working with different ampoules at one and the same temperature.

Moreover, after the experiments that were carried out at one partiocular temperature or another, but above 304° (end of transformation), so-called control experiments were also carried out at 240° which served to indicate the absence of chemical interaction between the material of the ampoule and NaOH at the heating temperatures that were employed.

The graph of the temperature dependence of the heat capacity of NaOH may be split into 3 sections.

The first takes in the interval 106.8-230° and is expressed by equations:

mean specific heat

$$\bar{c}^{t}_{p_{20}} = 0.3628 + 1.0094 \cdot 10^{-4} (t - 20); \qquad (21)$$

mean molar heat capacity

$$\bar{C}^{t}_{p_{20}} = 14.515 + 0.4038 \cdot 10^{-2} (t - 20); \qquad (22)$$

true molar heat capacity

$$C_p = 14.353 + 0.8076 \cdot 10^{-2}\, t. \qquad (23)$$

In the second section in temperature interval 230-295° the curve turns sharply upward at 230°, which indicates the beginning of a polymorphic transformation.

In the temperature interval 295-304.2° precise reproducibility of the enthalpy is not observed.

Evidently, in this interval the same transformation occurs that takes place to a differing degree in individual experiments.

An abnormal increase of the heat capacity of NaOH is observed in the temperature interval 304-315.6° and must be attributed to premelting processes.

The 3rd section takes in the interval of fused NaOH (329-742.8°) and is expressed by equations:

mean specific heat

$$\bar{c}^{t}_{p_{329}} = 0.5156 - 0.670 \cdot 10^{-4} (t - 329); \qquad (24)$$

mean molar heat capacity

$$\bar{C}^{t}_{p_{329}} = 20.627 - 0.268 \cdot 10^{-2}\,(t - 329); \tag{25}$$

true molar heat capacity

$$C_p = 22.390 - 0.536 \cdot 10^{-2}\,t. \tag{26}$$

The heat of fusion, referred to 303.6°, was calculated by Equation (12), Q = −1929.7 cal/mole. The heat of fusion, referred to 322°, was calculated also by Equation (12). Q = −1629.3 cal/mole for which in the given case the magnitude $\bar{c}_1(t_2-t_1)$ (enthalpy in the interval of melting and transformation temperatures) enters into the magnitude Q of Equation (12).

The literature contains very little data on heat capacity and enthalpy of solid and fused caustic soda. The earliest work [8] relates to solutions with a concentration of 50-100% NaOH for temperatures of 0-98°. Extrapolation of these data gave c_p = 0.9 cal/g · degree for the heat capacity of fused caustic soda. This heat capacity value cannot stand up under criticism and, as was shown even in its time [8], did not satisfy even the needs of technical calculation in working out the heat balance of the fusion process of NaOH.

Solid NaOH exists in two physical modifications (α and β). The heat of transformation of one form to another was not determined experimentally by anyone and is, as we showed, of considerable magnitude, greater than the heat of fusion, but the difference in the temperatures of fusion and transformation is small (about 19°).

Earlier, the mean heat capacity of NaOH was determined [9] in the temperature interval (100-19°) to be $\bar{c}_{p_{19}}^{100}$ = 0.3780 cal/g · degree. The preparation had the composition: NaOH 97.17%, Na_2CO_3 2.43%, H_2O 0.40%. The determinations were carried out in a massive calorimeter with an adiabatic casing developed by Skuratov.

This magnitude differed from ours for this temperature interval by less than 2%, which for such a substance as NaOH must be considered to be satisfactory agreement.

The literature [8] gives the mean heat capacity for five samples of fused caustic soda which contained from 2 to 19.7% soda. The determinations were carried out for the temperature interval t-330° where for the sample with 2% Na_2CO_3 t = 580°. Our data on fused NaOH differs from the data of [8] up to ± 5%.

The data of [8] are fully satisfactory for technical calculations. However, the initial increase in the heat capacity with temperature with its subsequent decrease given in this work, seems doubtful.

Chevesy [10] examined the cooling curve of NaOH and showed by calculation that the heat of fusion of NaOH is equal to 1602 cal/mole. The agreement of his data with ours is purely accidental, since in the magnitude that we determined, the enthalpy is included for the temperature interval: transformation temperature-fusion temperature (~19°), the magnitude of which is equal to approximately half of the given heat of fusion.

Chevesy also found by an indirect method that the heat of transformation of NaOH was equal to 990 cal/mole, which clearly does not agree with the experimental data of the present investigation (Q = −1930 cal/mole). Chevesy's data on heats of fusion and transformation entered into the reference literature. Our data introduce corrections for the data of Chevesy, which were obtained by an indirect method.

SUMMARY

1. The mean heat capacities of Na_2CO_3 were measured in the interval 20-1106.6°, those for Na_2SO_4 in the interval 20-1017.1° and those for NaOH in the interval 20-742.8°.

2. Equations were given for the calculation of the mean specific and true molar heat capacity of these substances. These equations show that due to the presence of polymorphic and phase transformations for Na_2CO_3, Na_2SO_4 and NaOH, corresponding coefficients have different values in different branches of the curves.

3. The heats of fusion of Na_2CO_3, Na_2SO_4 and NaOH were determined.

4. The heat of polymorphic transformation of α-NaOH and β-NaOH was determined.

5. It was found that near 320° Na_2CO_3 undergoes polymorphic transformation.

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2. [illegible] isotherms [illegible] and phase transformations [illegible], and NaOH [illegible] of the system.

3. The heats of [illegible] were determined.

4. The heat of polymorphic transformation of [illegible] was determined.

5. It was found that [illegible].

LITERATURE CITED

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[9] [illegible] J. Phys. Chem. [illegible]

[10] [illegible]

Received April [illegible], 1956

Moscow State University and [illegible]

Institute of [illegible]

Procedure

Fusion of the mixtures was carried out in glass test tubes in a muffle furnace with continuous mixing with a glass stirrer; the thermocouple was of nichrome-constantan. To avoid oxidation of the iodides, a stream of dry CO_2 was passed into the test tube through a capillary. In order to save space, part of the data obtained was not included in the table. All the compositional data are given in equimolar percentages.

Binary Systems

1. $PbCl_2-K_2Cl_2$. According to the literature data of [2], two compounds form in the system: $KCl \cdot 2PbCl_2$• with m.p. 440° and $PbCl_2 \cdot 2KCl$ which melts with decomposition; the transition point corresponds to 44.9% K_2Cl_2 and 400°.

According to our data, the fusion curve consists of four branches: K_2Cl_2, compound $2KCl \cdot PbCl_2$ melting with decomposition, $KCl \cdot 2PbCl_2$ melting without decomposition, and $PbCl_2$. The points of intersection of the branches are located at 490° and 46.5% K_2Cl_2, 410° and 32.5% K_2Cl_2, 421° and 12.5% K_2Cl_2. The curve has a clear maximum at 440° and 20% K_2Cl_2 (Figure 1, Table 1).

TABLE 1

$PbI_2-K_2I_2$		$PbCl_2-K_2Cl_2$		$K_2I_2-K_2Cl_2$	
% K_2I_2	Temperature	% K_2Cl_2	Temperature	% K_2I_2	Temperature
0.0	408°	0.0	496°	0.0	772°
5.0	391	5.0	475	10.0	746
10.0	376	10.0	439	20.0	705
12.5	364	12.5	421	30.0	653
15.0	347	15.0	428	40.0	600
17.5	327	17.5	434	50.0	586
20.0	327	20.0	440	55.0	584
22.5	342	25.0	437	60.0	587
25.0	349	30.0	421	70.0	599
27.5	353	32.5	411	80.0	638
30.0	356	35.0	426	90.0	668
32.5	358	40.0	454	100.0	680
35.0	362	45.0	482	—	—
40.0	405	47.5	501	—	—
45.0	455	50.0	530	—	—
50.0	503	60.0	596	—	—
		70.0	626		

TABLE 2

$PbCl_2-PbI_2$		Diagonal $PbI_2-K_2Cl_2$		Diagonal $PbCl_2-K_2I_2$	
% PbI_2	temperature	% K_2Cl_2	temperature	% K_2I_2	temperature
0.0	496°	0.0	408°	0.0	496°
5.0	473	10.0	371	5.0	432
10.0	454	12.0	361	7.5	399
20.0	422	13.0	351	10.0	390
30.0	396	15.0	336	12.5	381
35.0	380	17.5	318	15.0	367
40.0	365	20.0	304	20.0	342
45.0	360	22.5	285	23.0	330
50.0	362	25.0	287	25.0	327
55.0	361	27.5	304	27.5	342
60.0	360	30.0	321	30.0	354
65.0	355	32.5	353	32.5	360
67.5	349	35.0	376	35.0	380
70.0	344	40.0	421	37.5	412
72.5	336	50.0	502	40.0	432
75.0	340				
80.0	358				

2. $PbI_2-K_2I_2$. Compound $KI \cdot PbI_2$ forms in the system with m. p. 349°. The eutectic points correspond to 19% K_2I_2 at 321° and 36% K_2I_2 at 346° [4].

According to other data, in the system there also forms compound $KI \cdot 2PbI_2$ with m.p. 335° (eutectic points occur at 17% K_2I_2 and 310° and at 24% K_2I_2 and 325° [1].

Upon investigation of the system, we also established compound $KI \cdot PbI_2$ with m.p. 358° without decomposition. The eutectic points occur at 18% K_2I_2 and 330° and 35% K_2I_2 and 357° (Figure 1, Table 1).

3. $K_2I_2-K_2Cl_2$. It was studied previously [5]; it is characterized by continuous solid solutions of K[Cl, I]; the minumum on the fusion curve is located at 584° and 47.5% K_2Cl_2 (Figure 1, Table 1).

4. $PbCl_2-PbI_2$. The components form a simple eutectic (76% PbI_2 and 306°)[2]. According to our data, the liquidus curve consists of three branches: the branch of $PbCl_2$, the branch of compound $PbCl_2 \cdot PbI_2$ melting without decomposition with a maximum at 362° and 50% PbI_2, and the branch PbI_2. The points of intersection of the branches are located at 360° and 42% PbI_2, 334° and 73.5% PbI_2 (Figure 1, Table 1).

• For abbreviation the following letters are used to designate the compounds: $PbI_2 \cdot KI$ – A; $PbI_2 \cdot PbCl_2$ – B; $KCl \cdot 2PbCl_2$ – C; $PbCl_2 \cdot 2KCl$ – D; solid solutions K[Cl, I] – E; $PbI_2 \cdot KCl$ – F.

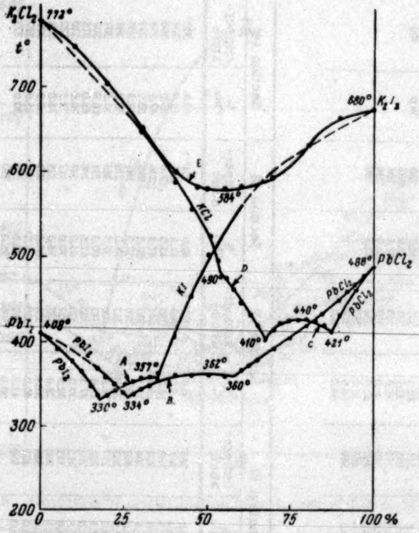

Fig. 1. Fusion curves of binary systems. Explanation in text.

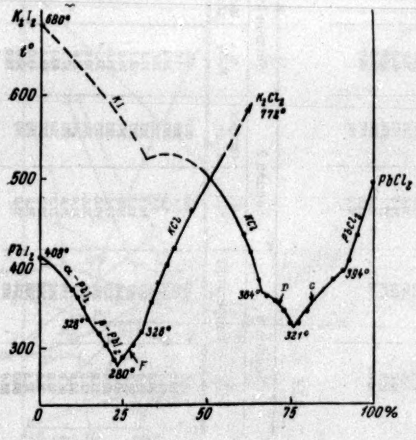

Fig. 2. Diagonal sections. Explanation in text.

TABLE 3

Section 1		Section 2		Section 3		Section 4		Section 5		Section 6		Section 7	
% K_2Cl_2	temperature	% K_2Cl_2	temperature	% K_2I_2	temperature	% K_2I_2	temperature	% $PbCl_2$	temperature	% $PbCl_2$	temperature	% K_2Cl_2	temperature
0.0	360°	0.0	362°	0.0	360°	0.0	363°	0.0	365°	0.0	349°	0.0	327°
2.5	354	5.0	344	5.0	335	5.0	342	5.0	361	2.5	340	5.0	321
5.0	346	10.0	323	7.5	318	10.0	315	10.0	356	5.0	336	10.0	315
7.5	333	12.5	318	10.0	309	15.0	291	15.0	352	7.5	328	12.5	313
10.0	321	15.0	315	15.0	304	17.5	284	20.0	342	10.0	320	15.0	311
15.0	321	17.5	314	20.0	291	20.0	278	22.5	338	12.0	311	17.5	307
20.0	319	20.0	311	25.0	282	22.5	278	25.0	328	15.0	303	20.0	331
25.0	325	22.5	307	27.5	300	25.0	288	27.5	327	17.5	293	25.0	376
30.0	355	25.0	318	30.0	318	27.5	311	30.0	321	20.0	280	30.0	420
35.0	380	30.0	342	35.0	346	30.0	335	32.5	321	25.0	282		
40.0	424	35.5	363	40.0	369	35.0	371	35.0	323	27.5	284		
45.0	470	37.5	378	45.0	383	40.0	399	40.0	327	30.0	284		
50.0	516	40.0	394	50.0	450	50.0	435	50.0	336	32.5	280		
		45.0	452	60.0	510	55.0	485	55.0	342				
		50.0	491			62.5	560	60.0	354				
								65.0	360				

TABLE 4

Section 8		Section 9		Section 10		Section 11		Section 12		Section 13		Section 14	
% $PbCl_2$	temperature	% K_2I_2	temperature	% K_2Cl_2	temperature	% K_2I_2	temperature	% K_2I_2	temperature	% PbI_2	temperature	% PbI_2	temperature
0.0	518°	0.0	367°	0.0	396°	0.0	365°	0.0	364°	40.0	331°	40.0	309°
10.0	437	2.5	358	5.0	369	5.0	351	5.0	358	42.5	325	42.5	304
17.5	370	5.0	347	10.0	349	7.5	340	10.0	353	45.0	316	45.0	300
20.0	356	7.5	342	15.0	360	10.0	320	15.0	344	47.5	306	47.5	294
25.0	367	10.0	327	17.5	360	12.5	304	17.5	333	50.5	295	50.0	293
30.0	367	12.5	307	22.5	358	15.0	289	18.5	328	52.5	282	52.5	296
40.0	340	15.0	291	26.0	355	17.5	283	20.0	313	55.0	278	55.0	289
50.0	300	17.5	283	25.0	353	20.0	277	22.5	306	57.5	285	57.5	302
55.0	295	19.0	273	27.5	355	22.5	283	25.0	313	60.0	291	60.0	307
57.5	293	20.0	280	30.0	376	25.0	292	27.5	320	62.5	298	65.0	315
60.0	311	21.0	284	35.0	405	27.5	315	30.0	325	65.0	307	70.0	320
65.0	338	25.0	293	37.5	418	30.0	342	32.5	327	70.0	317	72.5	322
70.0	355	27.5	310	40.0	430	32.5	360	35.0	333	75.0	325	76.0	328
75.0	366	30.0	327	42.5	460	35.0	380	37.5	338	80.0	339	80.0	339
77.5	366	32.5	352	45.0	493	40.0	405	40.0	380	85.0	356	85.0	357
80.0	374	35.0	373	50.0	537	45.0	430	45.0	452	90.0	371	90.0	373
85.0	403			55.0	567			50.0	500	95.0	390		

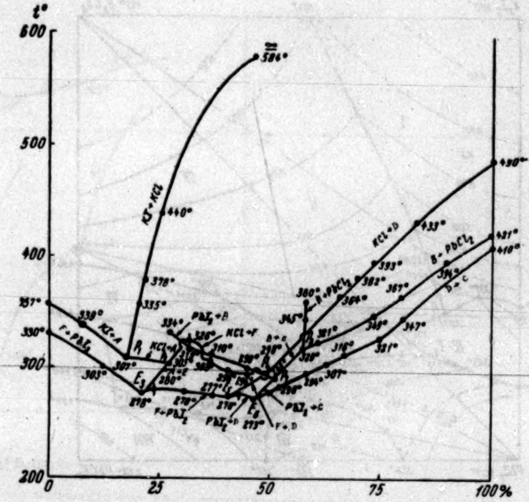

Fig. 3. Projection of crystallization of reciprocal system on side PbI_2-PbCl_2.

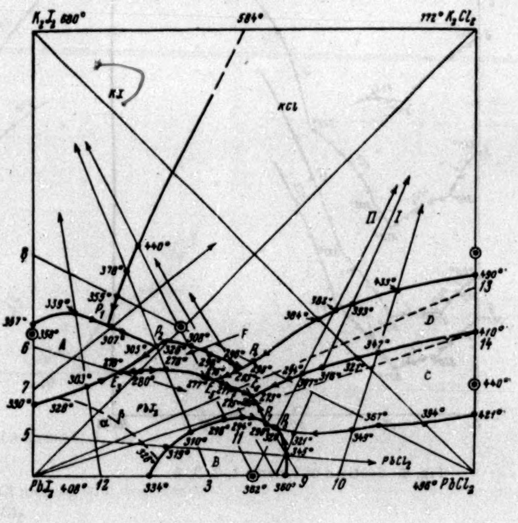
K_2I_2 680°
584°
772° K_2Cl_2
KI
KCl
8
6
7
5
387°
358°
339°
P1
355°
378°
440°
307°
A
303°
328°
330°
E3
278°
280°
305°
P2
326°
278°
308°
F
PbI2
α
β
298°
P3
E5
E6
277°
273°
319°
310°
298°
296°
11
P7
P8
321°
345°
B
PbI2 408°
12
334°
3
382°
380°
9
10
PbCl2
496° PbCl2
384°
388°
393°
433°
490°
13
D
410°
14
C
440°
347°
322°
316°
367°
394°
349°
421°
II
I

Fig. 4. Scheme of sectional distribution.

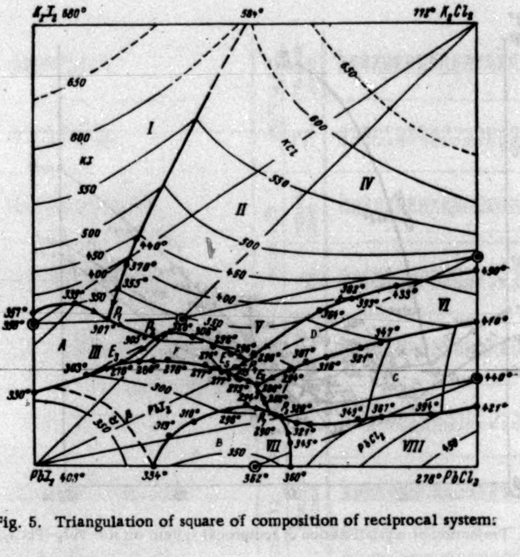
K_2I_2 680°
584°
778° K_2Cl_2
650
600
KI
550
500
450
400
350
I
II
III
IV
V
VI
VII
VIII
KCl
440°
378°
355°
339°
397°
PbI₂
PbCl₂
A
B
C
D
F
E_1
E_2
E_3
P_1
P_2
P_3
330°
303°
307°
278°
280°
313°
310°
298°
290°
321°
345°
349°
387°
394°
382°
393°
433°
490°
470°
440°
421°
PbI₂ 403°
334°
382°
360°
278° PbCl₂

Fig. 5. Triangulation of square of composition of reciprocal system:

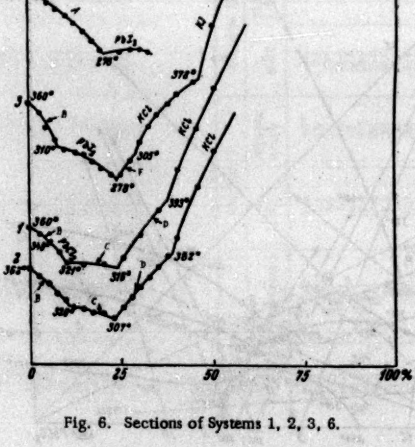

Fig. 6. Sections of Systems 1, 2, 3, 6.

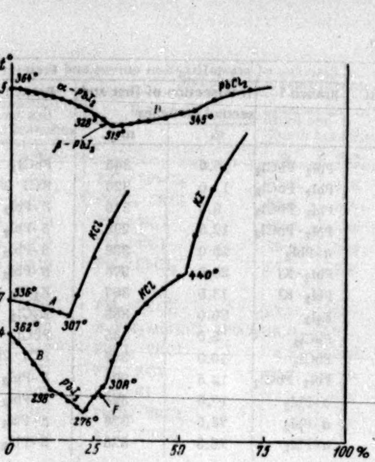

Fig. 7. Sections of Systems 4, 5, 7.

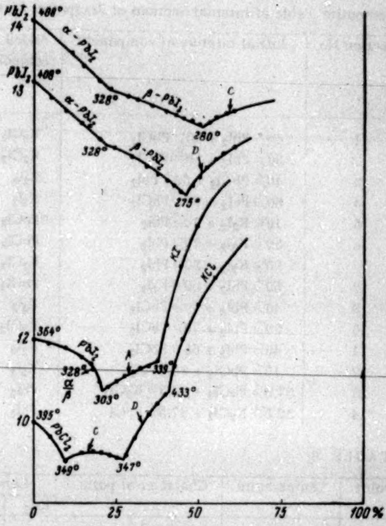

Fig. 9. Sections of Systems 10, 12, 13, 14.

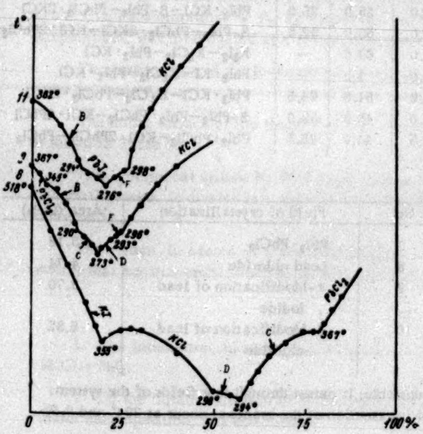

Fig. 8. Sections of Systems 8, 9, 11.

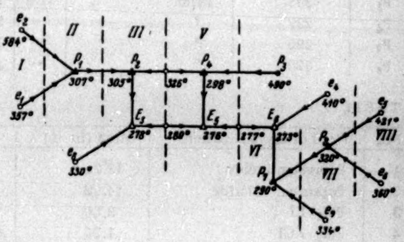
e₂
384°
I
II
III
V
P₁
P₂
P₄
P₃
307°
305°
326°
298°
400°
e₁
357°
E₁
E₃
E₂
278°
280°
276°
277°
273°
e₄
410°
e₃
e₈
330°
VI
P₅
481°
VIII
320°
VII
P₇
e₅
360°
290°
e₉
334°

Fig. 10. Scheme of crystallization of system K, Pb ∥ Cl, I.

Diagonal Sections

Stable diagonal section PbI_2—K_2Cl_2 (Figure 2, Table 2) intersects two fields of components (α- and β-PbI_2 and K_2Cl_2) and the field of the binary heterocompound $PbI_2 \cdot KCl$ melting with decomposition respectively at 328° and 15% K_2Cl_2, 280° and 28.5% K_2Cl_2, and 326° and 29.5% K_2Cl_2.

TABLE 5

Composite Table of Internal Sections of Reciprocal System.

Section No.	Initial mixture of component	Added component	Branches of crystallization curves and their intersections			
			Branch I	Intersection of first and second branches		Branch II
				%	m.p.	
1	45% PbI_2 + 55% $PbCl_2$	K_2Cl_2	$PbI_2 \cdot PbCl_2$	5.0	345	$PbCl_2$
2	50% PbI_2 + 50% $PbCl_2$	K_2Cl_2	$PbI_2 \cdot PbCl_2$	11.0	320	$KCl \cdot 2PbCl_2$
3	40% $PbCl_2$ + 60% PbI_2	K_2I_2	$PbI_2 \cdot PbCl_2$	9.0	310	β-PbI_2
4	50% PbI_2 + 50% $PbCl_2$	K_2I_2	$PbI_2 \cdot PbCl_2$	12.5	298	β-PbI_2
5	10% K_2I_2 + 90% PbI_2	$PbCl_2$	α-PbI_2	25.0	328	β-PbI_2
6	30% K_2I_2 + 70% PbI_2	$PbCl_2$	$PbI_2 \cdot KI$	20.0	278	β-PbI_2
7	20% K_2I_2 + 80% PbI_2	K_2Cl_2	$PbI_2 \cdot KI$	17.5	307	K_2Cl_2
8	50% PbI_2 + 50% K_2I_2	$PbCl_2$	K_2I_2	20.0	355	K_2Cl_2
9	40% PbI_2 + 60% $PbCl_2$	K_2I_2	$PbCl_2$	5.0	345	$PbCl_2 \cdot PbI_2$
10	30% PbI_2 + 70% $PbCl_2$	K_2Cl_2	$PbCl_2$	10.0	349	$KCl \cdot 2PbCl_2$
11	45% PbI_2 + 55% $PbCl_2$	K_2I_2	$PbI_2 \cdot PbCl_2$	13.5	294	β-PbI_2
12	15% $PbCl_2$ + 85% PbI_2	K_2I_2	α-PbI_2	17.5	328	β-PbI_2
13	57.5% $PbCl_2$ + 42.5% K_2Cl_2	PbI_2	α-PbI_2	76.5	328	β-PbI_2
14	32.5% K_2Cl_2 + 67.5% $PbCl$	PbI_2	α-PbI_2	76.5	328	β-PbI_2

TABLE 6

Point	Temperature	Character of point	Composition (in mol %)				Equilibrium phases
			K_2I_2	K_2Cl_2	PbI_2	$PbCl_2$	
E_3	278°	Eutectic	3.0	20.5	76.5	–	$PbI_2 \cdot KI$–β-PbI_2–$PbI_2 \cdot KCl$
E_5	276	Ditto	–	20.0	55.0	25.0	$PbI_2 \cdot KCl$–β-PbI_2–$PbCl_2 \cdot 2KCl$
E_6	273	"	–	18.0	50.0	32.0	β-PbI_2–$PbCl_2 \cdot 2KCl$–$KCl \cdot 2PbCl_2$
P_1	307	Transformation	16.0	17.0	67.0	–	K_2I_2–K_2Cl_2–$PbI_2 \cdot KCl$
P_2	305	Ditto	71.0	28.0	1.0	–	$PbI_2 \cdot KI$–K_2Cl_2–$PbI_2 \cdot KCl$
P_4	298	"	–	24.0	51.5	24.5	$PbI_2 \cdot KCl$–K_2Cl_2–$PbCl_2 \cdot 2KCl$
P_7	290	"	–	13.0	48.0	39.0	β-PbI_2–$PbI_2 \cdot PbCl_2$–$KCl \cdot 2PbCl$
P_8	320	"	–	10.5	44.0	45.5	$PbI_2 \cdot PbCl_2$–$KCl \cdot 2PbCl_2$–$PbCl_2$

TABLE 7

No.	Field of crystallization	Area (in %)	No.	Field of crystallization	Area (in %)
1	Potassium iodide	19.31	7	$PbI_2 \cdot PbCl_2$	3.18
2	Potassium chloride	44.72	8	Lead chloride	4.74
3	$PbI_2 \cdot KI$	3.50	9	α-Modification of lead iodide	3.70
4	$PbI_2 \cdot KCl$	1.20			
5	$PbCl_2 \cdot 2KCl$	6.50	10	β-Modification of lead chloride	5.32
6	$KCl \cdot 2PbCl_2$	7.83			

Diagonal section $PbCl_2$–K_2I_2 (Figure 2, Table 2) is unstable; it passes through four fields of the system: $PbCl_2$, $KCl \cdot 2PbCl_2$, $PbCl_2 \cdot 2KCl$ and K_2Cl_2. The points of intersection of the branches occur at 394° and 7.5% K_2I_2, 321° and 24.5% K_2I_2 and 364° and 34% K_2I_2.

14 sections in all were investigated (Figures 6-9, Tables 3-5).

Phase diagram of reciprocal system. Using the results of the investigation of binary systems, diagonals and 14 internal sections we constructed the projection of the co-crystallization curves on the plane of the polytherm of binary system PbI_2–$PbCl_2$ (Figure 2), which permitted a more accurate determination of the position

Branches of crystallization curves and their intersections

intersection of second and third branches		Branch III	intersection of third and fourth branches		Branch IV	intersection of fourth and fifth branches		Branch V	intersection of fifth and sixth branches	
%	m.p.		%	m.p.		%	m.p.		%	m.p.
10.0	321	$KCl \cdot 2PbCl_2$	23.0	316	$PbCl_2 \cdot 2KCl$	37.0	393	K_2Cl_2		
22.5	307	$PbCl_2 \cdot 2KCl$	38.5	382	K_2Cl_2					
24.0	278	$PbI_2 \cdot KCl$	28.5	305	K_2Cl_2	46.0	378	K_2I_2		
22.0	277	$PbI_2 \cdot KCl$	29.0	308	K_2Cl_2	52.0	440	K_2I_2		
80.0	319	$PbI_2 \cdot PbCl_2$	57.0	345	$PbCl_2$					
50.0	298	$PbI_2 \cdot 2KCl$	57.5	294	$KCl \cdot 2PbCl_2$	79.0	367	$PbCl_2$		
14.5	290	β-PbI_2 and $KCl \cdot 2PbCl_2$	18.0	273	$PbCl_2 \cdot 2KCl$	22.5	293	$PbI_2 \cdot KCl$	25.0	296
27.0	347	$PbCl_2 \cdot 2KCl$	4.0	433	K_2Cl_2					
25.0	277	$PbI_2 \cdot KCl$	27.0	298	K_2Cl_2					
21.0	303	$PbI_2 \cdot KI$	37.5	339	K_2I_2					
53.5	277	$PbCl_2 \cdot 2KCl$								
49.0	280	$KCl \cdot 2PbCl_2$								

of triple points and isothermal points on the co-crystallization curves and also permitted checking of the obtained experimental data (Table 5). The direction of the sections and the curves, delimiting the fields of crystallization of the individual salts and complexes, are given in Figure 4.

The surface of the liquidus consists of nine fields and one additional one, due to the presence of polymorphism of lead iodide (Figure 5). These fields converge to eight invariant points: three eutectics E_3, E_5 and E_6 and five transformations P_1, P_2, P_4, P_7 and P_8. The system, due to the decomposition of iodides at high temperatures, was investigated at a temperature not exceeding 500°.

The composition of the invariant points and the equilibrium phases, corresponding to these points, are given in Table 6.

The entire surface of the liquidus of the reciprocal system is distributed between fields of crystallization as shown in Table 7.

Thus, reciprocal system K, Pb ‖ Cl, I, triangulated by the diagonal cross section $PbI_2-K_2Cl_2$ and six adiagonal secants, is divided into eight phase triangles. A schematic representation of crystallization is given in Figure 10.

The system, in accord with the classification of A. G. Bergman and G. A. Bukhalova [6], is related to systems that are irreversible-reciprocal with an internal incongruent heterocompound.

SUMMARY

1. The interaction, in absence of solvent, was studied for irreversible-reciprocal system $2KI + PbCl_2 = 2KCl + PbI_2$.

2. On the liquidus diagram of binary system $PbCl_2-PbI_2$ the presence of complex $PbCl_2 \cdot PbI_2$, melting without decomposition, was established.

3. The surface of the liquidus of the reciprocal system consists of ten fields of crystallization.

4. The existence of a binary heterocompound of supposed composition $PbI_2 \cdot KCl$ was established. Its field of crystallization is intersected by stable diagonal $PbI_2-K_2Cl_2$.

5. The reaction of double decomposition in the investigated system predominates over complexformation.

6. The system is divided by seven triangulating secants into eight phase triangles.

7. System K, Pb || Cl, I, is classified as irreversible-reciprocal with an internal binary heterocompound.

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TERNARY SYSTEM OF FIVE IONS $Na_2CO_3 - K_2Cl_2 - K_2SO_4$

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Investigation of the quaternary reciprocal system of chlorides, sulfates and carbonates of sodium and potassium has as its object the investigation of the stability of solid solutions and of complex-formation between the most common and simplest salts of sodium and potassium in melts and also the study of low-melting alloys to be used as salt baths for thermal treatment, sulfidation and in melting special steels, etc.

In the ternary system we investigated, one side is the binary system $K_2Cl_2-K_2SO_4$ and the two other sides are $K_2Cl_2-Na_2CO_3$ and $Na_2CO_3-K_2SO_4$, which are stable diagonal cross-sections of the respective reciprocal systems (Fig. 1a).

Of special interest is the last reciprocal system Na, K ‖ CO_3, SO_4, which on all four lateral sides has continuous series of solid solutions which, however, inside the reciprocal system, partially break up along stable diagonal $Na_2CO_3-K_2SO_4$. The region of break-up of the homogeneous solid solutions of all the components, evidently, should form a lens-like region along stable cross-section $Na_2CO_3-K_2SO_4$.

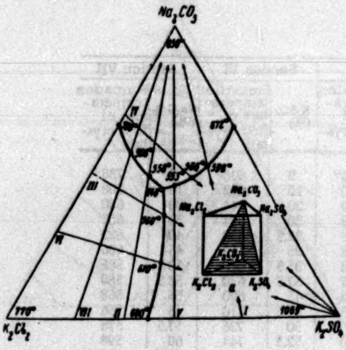

Fig. 1. Arrangement of internal sections in the system $Na_2CO_3-K_2Cl_2-K_2SO_4$.
a) Position of the ternary system inside the quaternary.

In the two cited reciprocal systems Na, K ‖ Cl, CO_3 and Na, K ‖ CO_3, SO_4 there are the following relative thermal effects to the side of the cited stable diagonals, namely +0.29 kcal/equiv. and −0.75 kcal/equiv. respectively; it must be noted that for the second system the relative heat effect is negative (−0.75 kcal/equiv.): however, the cross-sectional diagram shows it to be stable. In view of the fact that the heat effect is very small, it is possible that this slight contradiction is due to the inaccuracy of the thermal determinations. The direction of the reaction corresponds to the formation of the most refractory salt K_2SO_4 (1069°).

The investigated system showed the absence of additional interaction within itself; a ternary eutectic point was established in it.

EXPERIMENTAL

Procedure and starting substances. The investigation was carried out by the visual-polythermal method in a platinum crucible with a platinum stirrer; a Pt/Pt, Rh thermocouple was used. All the salts were carefully purified. To save space not all the experimental data were included in the tables. All the percentages are equimolar.

Lateral delimiting systems (Fig. 2, Table 1). $K_2Cl_2-K_2SO_4$ was investigated a number of times previously. According to our data, the eutectic point corresponds to 690° (58.5% K_2Cl_2). On the K_2SO_4 curve, discontinuities stand out quite clearly at 740° (51% K_2Cl_2) and 850° (33.5% K_2Cl_2). These transformations were

TABLE 1

Lateral Delimiting Systems and Sections I and II

K_2Cl_2—K_2SO_4		K_2SO_4—Na_2CO_3		K_2Cl_2—Na_2CO_3		Section I		Section II.	
K_2SO_4 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals
0	770°	0	1069°	0	770°	0	884°	0	704°
10	758	10	1030	10	740	10	828	10	678
20	738	20	980	20	706	20	766	20	646
30	716	30	908	30	676	25	740	30	616
32.5	710	35	870	35	660	30	712	35	600
35	705	40	832	40	646	35	684	40	586
37.5	700	45	794	45	634	40	658	45	572
40	694	50	760	50	620	45	634	47.5	564
41.5	690	52.5	744	55	608	50	610	49.5	558
42.5	694	55	728	60	596	52	598	50	562
45	712	60	700	62.5	590	52.5	602	52.5	574
47.5	728	65	676	63	588	55	614	57.5	610
50	744	66	672	65	606	57.5	624	60	614
55	780	67.5	686	70	654	60	636	62.5	628
60	816	75	738	75	700	62.5	650	65	640
65	848	85	792	80	734	65	662	70	672
70	884	100	850	95	766	70	690	75	704

TABLE 2

Sections Through the Ternary System

Section III		Section IV		Section V		Section VI		Section VII	
K_2SO_4 (%)	Formation temperature of first crystals	K_2SO_4 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals	K_2SO_4 (%)	Formation temperature of first crystals	Na_2CO_3 (%)	Formation temperature of first crystals
0	620°	0	654°	0	744°	0	676°	0	738°
10	606	10	626	10	700	10	662	10	708
20	585	20	598	20	660	20	644	20	680
25	572	25	580	25	638	30	624	30	652
27.5	564	27.5	574	30	618	32.5	618	40	622
28.5	560	30	566	32.5	608	35	612	45	606
30	568	32.5	590	35	598	35.5	610	50	588
32.5	584	40	654	37.5	588	37.5	630	52.5	580
35	600	42.5	674	45	558	45	690	55	568
37.5	620	45	690	46	553	47.5	710	56	566
45	678	47.5	710	47.5	560	50	726	57.5	576
47.5	696	50	730	55	590	52.5	744	60	598
50	716	52.5	750	57.5	600	55	762	62.5	616
52.5	734	55	770	60	612	60	802	65	634
55	754	60	810	62.5	624	65	836	67.5	650
60	794	65	848	70	664	70	872	70	668
65	840	75	924	75	692	75	910	75	704

mentioned a number of times recently in our investigation. Below the eutectic horizontal a polymorphic transformation is apparent at 590°.

K_2Cl_2—Na_2CO_3 was investigated previously [1, 2]; according to our data the eutectic corresponds to 588° (33.5% K_2Cl_2). The fusion curve of Na_2CO_3 shows transformations at 604 and 640°, which are, evidently, homeomorphic.

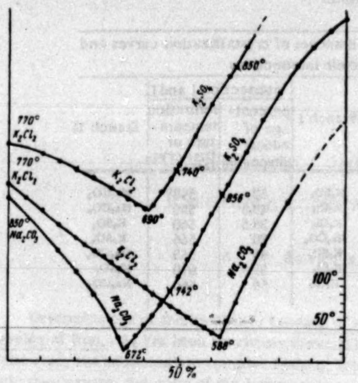

Fig. 2. Binary lateral sides of triple system Na, K ‖ Cl, SO_4, CO_3.

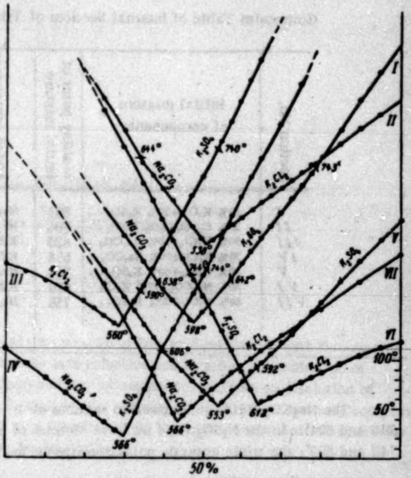

Fig. 3. Internal sections of system Na, K ‖ Cl, SO_4, CO_3.

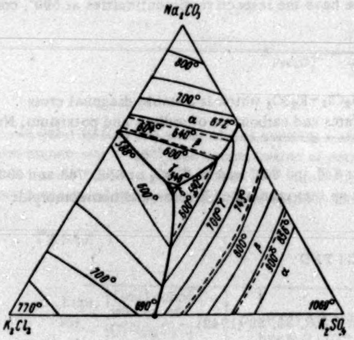
Na_2CO_3
800°
700°
α
672°
700°
640°
β
600°
508°
600°
590°
700° γ
745°
800°
β
900°
α
700°
770°
690°
1069°
K_2Cl_2
K_2SO_4

Fig. 4. Projection of composition diagram of system Na, K ‖ Cl, SO_4, CO_3 on triangle of composition.

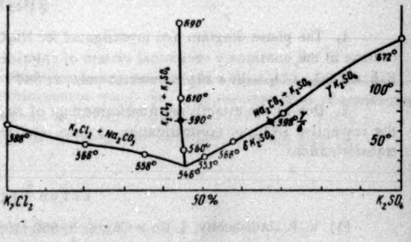

Fig. 5. Projection of curves of co-crystallization of system Na, K ‖ Cl, SO_4, CO_3.

According to our data, the eutectic point of $Na_2CO_3-K_2SO_4$ corresponds to 672° (34% K_2SO_4). In this system, apparently, we have two terminal solid solutions.

Triple system $Na_2CO_3-K_2Cl_2-K_2SO_4$. Seven internal sections were investigated (Figures 1, 3, Tables 1, 2).

The composite data with points of intersection of the crystallization curves are given in Table 3. The crystallization surface (Fig. 4) consists of three fields that occupy the following portions of the area of the triangle: K_2SO_4 43%, K_2Cl_2 36.3% and Na_2CO_3 20.7%.

TABLE 3

Composite Table of Internal Sections of Triple System

Section No.	Initial mixture of components	Melting point of initial mixture	Added component	Branches of crystallization curves and their intersections			
				Branch I	Intersection I and II		Branch II
					percentage of added component	formation temperature of first crystals	
I	30% K_2Cl_2+70% K_2SO_4 . .	884°	Na_2CO_3	K_2SO_4	52	598°	Na_2CO_3
II	35% K_2SO_4+65% K_2Cl_2 . .	704	Na_2CO_3	K_2Cl_2	49.5	558	Na_2CO_3
III	50% K_2Cl_2+50% Na_2CO_3 .	620	K_2SO_4	K_2Cl_2	28.5	560	K_2SO_4
IV	30% K_2Cl_2+70% Na_2CO_3 .	654	K_2SO_4	Na_2CO_3	30	566	K_2SO_4
V	50% K_2Cl_2+50% K_2SO_4 . .	744	Na_2CO_3	K_2SO_4	46	553	Na_2CO_3
VI	30% Na_2CO_3+70% K_2Cl_2 .	676	K_2SO_4	K_2Cl_2	35.5	610	K_2SO_4
VII	80% K_2Cl_2+20% K_2SO_4 . .	738	Na_2CO_3	K_2Cl_2	56	566	Na_2CO_3

The Na_2CO_3 field subdivides into sections of α, β, and γ homeomorphic modifications, split by isotherms of 640 and 604°. In the K_2SO_4 field we have sections of α, β, γ and δ-modifications, split by isotherms of 856, 743 and 590°; the triple eutectic point corresponds to 546° (31% K_2Cl_2 + 44.5% K_2SO_4 + 24.5% Na_2CO_3).

As can be seen from the projection of the crystallization surface on side $K_2Cl_2-K_2SO_4$ (Fig. 5), on the curve of co-crystallization of $Na_2CO_3-K_2SO_4$ and $K_2Cl_2-K_2SO_4$, we have the respective discontinuities at 590°, corresponding to the polymorphic transformation of K_2SO_4.

SUMMARY

1. The phase diagram was investigated for $Na_2CO_3-K_2Cl_2-K_2SO_4$ which is a stable diagonal cross section of the quaternary reciprocal system of chlorides, sulfates and carbonates of sodium and potassium, Na, K ‖ Cl, SO_4, CO_3 with a triple eutectic point at 546°.

2. Due to the established transformations of Na_2CO_3 at 640 and 604° and of K_2SO_4 at 856, 743 and 590°, the respective fields of crystallization of these salts are split up into sections of hetero- and homeomorphic transformations.

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OXALATE COMPLEXES OF IRON (III)

II. INSTABILITY CONSTANT AND EQUILIBRIUM DIAGRAM

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Determination of the instability constant of monooxalate complex of iron by equilibrium with thiocyanate complex of iron. As has been previously shown [1], in strongly acid solutions and at a low concentration of oxalic acid, the monooxalate complex $FeC_2O_4^+$ forms. Upon addition of ammonium oxalate to a solution of ferric thiocyanate, the color of the latter weakens due to formation of a colorless (at low concentrations) complex of iron (III). On the basis of the change of optical density as a function of the oxalate-ion concentration, the instability constant of the monooxalate complex of iron may be determined.

The first instability constant has the form:

$$K_{FeC_2O_4^+} = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]}. \qquad (1)$$

In order to find the value of this constant a series of experiments was carried out: the total concentration of iron nitrate was $4 \cdot 10^{-4}$, the concentration of potassium thiocyanate was $4 \cdot 10^{-3}$, the concentration of ammonium oxalate varied from $0.4 \cdot 10^{-3}$ to $3.6 \cdot 10^{-3}$ mole/liter. The concentration of nitric acid was 0.5 N. Table 1 gives the results of the measurements of optical-density (D) and the subsequent calculations of the constant.

TABLE 1

Expt. No.	Total concentration of $(NH_4)_2C_2O_4$ (mole/l · 10^4)	D	$[Fe^{3+}] = [FeSCN^{2+}]$ (mole/l · 10^4)	$[FeC_2O_4^+]$ (mole/l · 10^4)	$[C_2O_4^{2-}]$ · (mole/l · 10^4)	$K_1 = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]}$ ($\cdot 10^4$)
1	—	0,61	(2)	—	—	—
2	1	0.47	1.54	0.92	1.23	2.06
3	2	0.40	1.30	1.40	2.51	2.33
4	3	0.31	1.00	2.00	3.78	1.89
5	4	0.27	0.88	2.24	5.10	2.00
6	6	0.22	0.72	2.56	7.75	2.18
7	8	0.19	0.62	2.76	10.42	2.34
8	10	0.16	0.52	2.96	13.10	2.30
9	12	0.14	0.46	3.08	15.78	2.36
10	16	0.12	0.40	3.20	21.17	2.64
11	20	0.09	0.30	3.40	26.54	2.34

The constant may be calculated by a simplified method. Using the data of this series of experiments, we select (or find by graphical interpolation) that experiment in which the decrease in optical density ($\overline{D}$) amounts to half of the initial, $\overline{D} = \frac{1}{2} D_0$, i.e., the concentration of $FeSCN^{2+}$ decreases by 50%. At a concentration

$$[SCN^-] = K_{FeSCN^{2+}} \tag{2}$$

always half of the iron, not bound in the oxalate complex, is present in a free state and half is bound in the complex $FeSCN^{2+}$. Therefore, when the optical density has decreased to one half, the added oxalate under the given conditions has bound half of the initial quantity of $FeSCN^{2+}$ and the same amount of free ferric ions in the $FeC_2O_4^+$ complex. In connection with this (when $\overline{D} = 0.5\ D_0$) it is apparent that the concentration of oxalate complex of iron is twice as great as the equilibrium concentration of the thiocyanate complex:

$$[FeC_2O_4^+] = 2\,[FeSCN^{2+}]. \tag{3}$$

The equilibrium constant of reaction

$$FeSCN^{2+} + C_2O_4^{2-} \rightleftharpoons FeC_2O_4^+ + SCN^- \tag{4}$$

is equal to

$$K_{\text{equil.}\,(4)} = \frac{[FeC_2O_4^+][SCN^-]}{[FeSCN^{2+}][C_2O_4^{2-}]} = \frac{K_{FeSCN^{2+}}}{K_{FeC_2O_4^+}}. \tag{5}$$

From which

$$K_{FeC_2O_4^+} = \frac{K_{FeSCN^{2+}}}{K_{\text{equil.}\,(4)}} = \frac{K_{FeSCN^{2+}}\,[FeSCN^{2+}][C_2O_4^{2-}]}{[FeC_2O_4^+][SCN^-]} \tag{6}$$

Conditions (2) and (3) greatly simplify Equation (6), since we therefore have:

$$K_{FeC_2O_4^+} = \frac{[C_2O_4^{2-}]}{2}. \tag{7}$$

Thus, under the cited conditions the value of the instability constant of the iron-oxalate complex is numerically equal to half of that concentration of oxalate ion at which the initial color of the ferric thiocyanate decreases to half its original intensity. Thus, for example, in the series of experiments (Table 1) the color intensity decrease (to half of the initial) of $FeSCN^{2+}$ takes place at a concentration $[(NH_4)_2C_2O_4] = 3.1 \cdot 10^{-8}$. Upon accounting for $[(NH_4)_2C_2O_4^0]$, $[FeC_2O_4^+]$ and $[H^+]$, we find $[C_2O_4^{2-}]$, and then the instability constant:

$$K_{FeC_2O_4^+} = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]} = \frac{[C_2O_4^{2-}]}{2} = \frac{3.92 \cdot 10^{-8}}{2} = 1.96 \cdot 10^{-8}.$$

For more precise calculation of the instability constant it is necessary, according to (1), to know the concentrations $[Fe^{3+}]$, $[FeC_2O_4^+]$ and $[C_2O_4^{2-}]$. These values were given in Columns 4, 5 and 6 in Table 1. Calculation of these values is carried out as follows. The concentration of $[SCN^-]$ considerably exceeds the total concentration of iron, and may therefore be considered constant. For simplification of the calculations the concentration of potassium thiocyanate in all experiments was taken to be numerically equal to the value of the instability constant of iron monothiocyanate:

$$[SCN^-] = K_{FeSCN^{2+}} = 4 \cdot 10^{-3}. \tag{8}$$

Under these conditions always $\frac{[Fe^{3+}]}{[FeSCN^{2+}]} = \frac{1}{1}$, i.e., half of the iron, not bound in some other (in the given case oxalate) complex, will be present in the form of ferric thiocyanate, and half will be in the free state. The concentration of $[FeSCN^{2+}]$ was calculated from the optical density data. Under the conditions of Experiment 1, when the oxalate ion is absent, at $[SCN^-] = K_{FeSCN^{2+}} = 4 \cdot 10^{-3}$ [7] half the iron is bound in the thiocyanate complex, i.e.

$$[Fe^{3+}] = [FeSCN^{2+}] = \frac{1}{2}\,[Fe_{tot.}]. \tag{9}$$

Upon addition of ammonium oxalate, the thiocyanate complex is broken up, due to the formation of a more stable, colorless iron-oxalate complex. Hence, the concentration of ferric thiocyanate in Experiments 2, 3, etc. decreases proportionally to the decrease in optical density of the initial solution, i.e., having in mind (9):

$$[FeSCN^{2+}] = \frac{D_n}{D_1}\,[FeSCN^{2+}]^{*} = \frac{D_n}{D_1} \cdot \frac{Fe_{tot.}}{2},$$

in which $[Fe_{tot.}]$ designates, as in Equation (9), the sum of the concentrations of ferric thiocyanate and the free ferric ions in equilibrium with it; D_n is the optical density of the given solution under investigation, D_1 is the optical density of the first solution (in absence of oxalate ion). Thus, for example, for Experiment 2 (Table 1) the concentration of ferric thiocyanate is:

$$[FeSCN^{2+}] = \frac{0.47 \cdot 4 \cdot 10^{-4}}{0.61 \cdot 2} = 1.54 \cdot 10^{-4}.$$

The concentration of $[FeC_2O_4^+]$ is equal to the decrease in the concentration of $[FeSCN^{2+}]$ $(\overline{C})$ multiplied by two, since in accord with the above-cited condition, half of the iron not bound in the oxalate complex remains in the free state and half is bound in $FeSCN^{2+}$. That is, in general form:

$$\overline{C} = \underset{\text{expt. 1}}{[FeSCN^{2+}]} - \underset{\text{expt. "n"}}{[FeSCN^{2+}]}.$$

In the case of Experiment 2 we have: $\overline{C} = 2 \cdot 10^{-4} - 1.54 \cdot 10^{-4} = 0.46 \cdot 10^{-4}.$

Hence,

$$[FeC_2O_4^+] = 2 \cdot \overline{C} = 2 \cdot 0.46 \cdot 10^{-4} = 0.92 \cdot 10^{-4}. \tag{9a}$$

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[*] From Experiment 1 (Table 1).

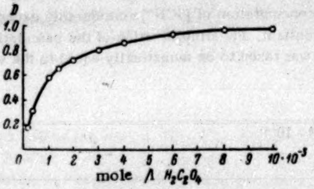

Figure 1. Dependence of the light-absorption by the complex on concentration of oxalic acid.

The concentration of free anions $[C_2O_4^{2-}]$ is calculated as follows. The oxalic acid not bound in the complex is designated by $S_{H_2C_2O_4}$. The hydrogen ion concentration is established by addition of nitric acid (0.5 N). The equilibrium concentration of unbound oxalate ions may be calculated [2], taking into account the total concentration of free oxalic acid, the hydrogen-ion concentration, and the dissociation constant of oxalic acid [3]:

$$[C_2O_4^{2-}] = S_{H_2C_2O_4}\frac{K'_aK''_a}{[H^+]^2+K'_a[H^+]+K'_aK''_a}\,. \tag{9b}$$

The calculated values of the instability constant are given in the last column of Table 1. The mean of all experiments:

$$K_1 = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]} = 2.2\,(\pm 0.2)\cdot 10^{-8}. \tag{10}$$

Determination of the instability constant of iron monooxalate by measuring the light-absorption in the ultraviolet region of the spectrum. A series of experiments was carried out in which the total concentration of ferric perchlorate was $5\cdot 10^{-4}$ M, the total concentration of oxalic acid varied from $0.2\cdot 10^{-3}$ to $10\cdot 10^{-3}$ M, and the concentration of perchloric acid was 0.5 N. The optical density was measured on a spectrophotometer (SF-4) at 302 mμ and a cell thickness of 9.997 mm. The solutions for comparison were prepared thusly: one cell was filled with a solution of ferric perchlorate and the other, standing in sequence with respect to the direction of the light, was filled with oxalic acid. The results are given in Table 2.

As can be seen from Fig. 1, with a sufficient excess of oxalic acid, namely at a concentration of about $8\cdot 10^{-3}$ mole/liter, the light-absorption practically does not change. It may be assumed that at this concentration of oxalic acid, the iron is completely bound in complex.

The concentration of ferric oxalate may be calculated by the equation: $FeC_2O_4^+ = \frac{D_1}{D_n}[Fe^{3+}_{tot.}]$, in which D_n is the optical density of the last experiment and D_1 is the optical density of the given experiment.

The concentration of $[Fe^{3+}]$ will be equal to the difference between the total concentration of iron and of $[FeC_2O_4^+]$. Then, taking into consideration the pH of the solution, the total concentration of $[H_2C_2O_4]$, and the acid dissociation constant of oxalic acid, we find the concentration of oxalate ion:

$$[C_2O_4^{2-}] = ([H_2C_2O_4]_{tot} - [FeC_2O_4^+])\frac{K'_aK''_a}{[H^+]^2+K'_a[H^+]+K'_aK''_a}\,.$$

The calculated values of $[FeC_2O_4^+]$, $[Fe^{3+}]$ and $[C_2O_4^{2-}]$ for all the experiments are given in Columns 3, 4 and 5, respectively, of Table 2. Knowing these values, it is possible to calculate the dissociation constant of iron monooxalate (last column of Table 2).

The mean value of the instability constant is:

$$K_{FeC_2O_4^+} = 0.7\,(\pm 0.06)\cdot 10^{-8}. \tag{11}$$

TABLE 2

$[H_2C_2O_4]$ (mole/l · 10^3)	D	$[FeC_2O_4^+]$ (mole/l · 10^3)	$[Fe^{3+}]$ (mole/l · 10^3)	$[C_2O_4^{2-}]$ (mole/l · 10^3)	$K_1 = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]} (\cdot 10^{8})$
0.2	0.185	0.096	0.40	0.14	0.58
0.4	0.317	0.16	0.34	0.32	0.68
1.0	0.579	0.30	0.20	0.95	0.63
1.4	0.650	0.34	0.16	1.43	0.67
2.0	0.722	0.37	0.13	2.19	0.73
3.0	0.795	0.41	0.09	3.50	0.77
4.0	0.855	0.44	0.06	4.81	0.66
5.0	0.886	0.46	0.04	6.13	0.53
8.0	0.960				
10.0	0.960				

The obtained value of the constant is quite near that of (10). Taking into account the simpler character of the equilibrium in the last series of experiments, we consider the value of (11) to be more accurate.

Conditions of formation of complexes $[Fe(C_2O_4)_2^-]$ and $[Fe(C_2O_4)_3^{3-}]$. Upon increasing the pH of the solution and also upon increasing the concentration of oxalate ions, the number of coordinated $C_2O_4^{2-}$ ions will increase and the following processes will take place in the system:

$$FeC_2O_4^+ + C_2O_4^{2-} = Fe(C_2O_4)_2^-,$$

$$Fe(C_2O_4)_2^- + C_2O_4^{2-} = Fe(C_2O_4)_3^{3-}.$$

The instability constant $K_{Fe(C_2O_4)_2^-} = \frac{[FeC_2O_4^+][C_2O_4^{2-}]}{[Fe(C_2O_4)_2^-]}$ characterizes the energy of the bond between the $FeC_2O_4^+$ and $C_2O_4^{2-}$ ions, and the instability constant $K_{Fe(C_2O_4)_3^{3-}} = \frac{[Fe(C_2O_4)_2^-][C_2O_4^{2-}]}{[Fe(C_2O_4)_3^{3-}]}$ characterizes the energy of the bond between $Fe(C_2O_4)_2^-$ and $C_2O_4^{2-}$. The values of these step-wise dissociation constants for iron-oxalate complexes were calculated by the method suggested by one of us [4]:

$$pK_2 : pK_1 = 0.67, \tag{a}$$

$$pK_3 : pK_2 = 0.27. \tag{b}$$

Using the data of Lambling [6], we find $pK_2 : pK_1 = 6.8 : 9.4 = 0.72$; $pK_3 : pK_2 = 4 : 6.8 = 0.59$.

Thus, the theoretical and experimental ratios of the step-wise constants almost coincide for $Fe(C_2O_4)_2^-$ and markedly differ for $Fe(C_2O_4)_3^{3-}$. Taking the mean values of the ratios between the step-wise constants and also the experimentally found first constant (11), we find: $pK_2 = 0.7 \cdot 8.2 = 5.8$; $pK_3 = 0.4 \cdot 5.8 = 2.3$. Hence,

$$K_2 = \frac{[FeC_2O_4^+][C_2O_4^{2-}]}{[Fe(C_2O_4)_2^-]} = 1.6 \cdot 10^{-6},$$

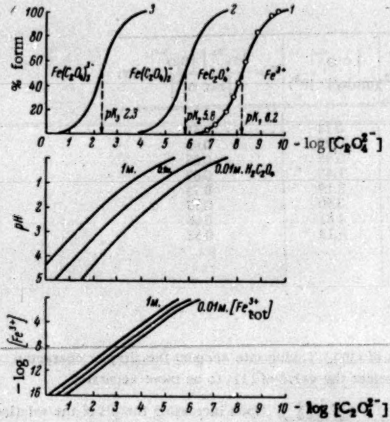

Figure 2. Equilibrium diagram of iron-oxalate complexes in solution.

$$K_3 = \frac{[Fe(C_2O_4)_2^-][C_2O_4^{2-}]}{[Fe(C_2O_4)_3^{3-}]} = 5 \cdot 10^{-3}.$$

The product of the dissociation constants $K = K_1K_2K_3 = 5.3 \cdot 10^{-17}$.

Equilibrium diagram of iron-oxalate complexes in solution. On the basis of the values of the dissociation constants it is possible to compose an equilibrium diagram for iron-oxalate complexes.

The upper part of Fig. 2 gives the distribution of the total concentration of iron $[Fe^{3+}_{tot.}]$ between the individual forms as a function of the oxalate-ion concentration. The values of $-\log [C_2O_4^{2-}]$ are shown on the abscissa axes. The ordinates are the relative quantities of the different complex forms. The curve, delineating regions of Fe^{3+} and $FeC_2O_4^+$, was calculated according to the equation

$$K_1 = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]}.$$

The binding of half of the iron in complex, i.e. $[Fe^{3+}] = [FeC_2O_4^+]$, takes place at $[C_2O_4^{2-}] = K_1 = 0.7 \cdot 10^{-8}$, i.e., at $pK_1 = pC_2O_4^{2-} = 8.2$. Analogously, according to K_2, we calculated the curve that delineates the regions $FeC_2O_4^+$ and $Fe(C_2O_4)_2^-$. The curve that delineates the regions $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$ was calculated by K_3. The mean graph of Fig. 2 shows the dependence of $-\log [C_2O_4^{2-}]$ on the total concentration of oxalic acid and on the pH of the solution. This dependence was calculated according to Equation (9b). The lower portion of the nomogram represents the dependence of the concentration of free ferric ion on the concentration of oxalate ion and also on the total iron concentration. The curves were calculated by the equation derived previously for salicylate complexes:

$$[Fe^{3+}_{free}] = [Fe^{3+}_{tot}] \frac{K_1K_2K_3}{[C_2O_4^{2-}]^3 + K_1[C_2O_4^{2-}]^2 + K_1K_2[C_2O_4^{2-}] + K_1K_2K_3},$$

in which K_1, K_2 and K_3 are the respective step-wise constants of the iron-oxalate complexes.

Curves 1, 2 and 3 of the upper portion of Fig. 2 are corroborated by the experimental data. The circles of Curve 1 represent the experimental points obtained at a constant concentration of ferric ion and an increasing concentration of oxalate ion; the hydrogen-ion concentration in these experiments was equal to 0.5 g-ion/liter. Upon increasing the oxalate-ion concentration, the iron is completely bound in $FeC_2O_4^+$.

The transition of $FeC_2O_4^+$ to $Fe(C_2O_4)_2^-$ was corroborated via ion-transfer determination during electrolysis. It turned out that at $[(NH_4)_2C_2O_4] < 1 \cdot 10^{-4}$ mole/liter (concentration of iron nitrate was $0.4 \cdot 10^{-4}$ mole/liter, $[HNO_3] = 0.02$), iron was detected only in the catholyte. At $[(NH_4)_2C_2O_4] > 2 \cdot 10^{-4}$ mole/liter iron was detected in the anolyte which indicates the formation of a complex anion. The presence of the complex anion $Fe(C_2O_4)_2^-$ was also demonstrated experimentally by the method of isomolar series, as demonstrated in the preceding communication.

The existence of complex compounds of the type $Me_3[Fe(C_2O_4)_3]$ (where Me = K, Na, NH_4^+) has been known for a long time [6].

SUMMARY

1. The dissociation constant of iron monooxalate has been determined by equilibrium with the colored (thiocyanate) iron complex. A simplified method of calculating the constant is suggested.

2. An improved procedure is presented for determining the instability constant of iron monooxalate by measuring the light-absorption in the ultraviolet region of the spectrum.

$$K_{FeC_2O_4^+} = \frac{[Fe^{3+}][C_2O_4^{2-}]}{[FeC_2O_4^+]} = 0.7\,(\pm 0.06) \cdot 10^{-8}.$$

3. The values of the step-wise dissociation constants have been determined for the iron-oxalate complex:

$$K_{Fe(C_2O_4)_2^-} = \frac{[FeC_2O_4^+][C_2O_4^{2-}]}{[Fe(C_2O_4)_2^-]} = 1.6 \cdot 10^{-6},$$

$$K_{Fe(C_2O_4)_3^{3-}} = \frac{[Fe(C_2O_4)_2^-][C_2O_4^{2-}]}{[Fe(C_2O_4)_3^{3-}]} = 5 \cdot 10^{-3}.$$

4. The conditions (concentration of oxalate-ion excess and pH of solution) under which iron is present in the form of $FeC_2O_4^+$, $Fe(C_2O_4)_2^-$ or $Fe(C_2O_4)_3^{3-}$ have been determined. The formation of $Fe(C_2O_4)_2^-$ has been corroborated by study of ion-transfer during electrolysis.

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COMPLEX COMPOUNDS OF PHOSPHORUS PENTACHLORIDE WITH CHLORIDES OF CERTAIN ELEMENTS

III. STUDY OF SYSTEMS PCl_5–HCl–ORGANIC SOLVENT

Ya. A. Fialkov and Ya. B. Buryanov

Study of the complex compounds of phosphorus pentachloride with chlorides of aluminum, trivalent iron [1] and certain other metals [2] showed that phosphorus enters into their composition as the cation $[PCl_4]^+$ and that their composition may be expressed by the general formula $[PCl_4]^+_m [MCl_{n+m}]^{m-}$.

The structure of the crystal lattice of phosphorus pentachloride, which consists of tetrahedral PCl_4^+ ions and octahedral PCl_6^- [3] anions, leads us to suppose that PCl_5 may also form complex halides of another type in which it is contained in the form of PCl_6^- ions. However, the literature lacks convincing data on the preparation of such complex compounds in their state, as compounds, or on their formation in solutions.

The first unsuccessful attempts to prepare compounds of PCl_5 with chlorides of alkali metals were those of Cronander [4]. Then Gutmann [5], while studying the possibility of preparing hexachlorophosphates, $MPCl_6$, showed that PCl_5 does not form compounds with potassium chloride upon direct reaction, even upon heating in a sealed tube for 20 hours at 200-450°. However, such a reaction takes place when this reaction is carried out in iodine chloride as a solvent [6]. This conclusion is based on the fact that upon conductometric titration of a PCl_5 solution with KCl solution in iodine chloride, the somewhat more rapid increase in conductivity, detected after attaining an equimolar KCl : PCl_5 ratio was ascribed [6] to the formation of the complex $KPCl_6$. This author uses concepts of the solvate theory, assuming that in the given case the reaction takes place between $KICl_2$ complexes (base in iodine chloride) and $PCl_5 \cdot ICl$. In order that the latter complex, for which the structure $[PCl_4]^+[ICl_2]^-$ [7, 8] was established, might play the role of the "acid" in iodine chloride, the author relates it to "amphoteric" substances and he expresses the above-cited reaction by the equation:

$$K^+ICl_2^- + I^+PCl_6^- \rightleftarrows K^+PCl_6^- + 2ICl. \qquad (1)$$

The author does not give any direct proof of the formation of $KPCl_6$ in the given system. The incorrectness of his ideas concerning the amphoteric character of the complex $PCl_5 \cdot ICl$ was already noted by one of us [9].

An attempt was also made to prepare $KPCl_6$ by means of the reaction of equimolar quantities of the complexes $KCl \cdot ICl$ and $PCl_5 \cdot ICl$ in iodine chloride with subsequent extraction of the resultant mass by dehydration of CCl_4 [5]. The residue contained phosphorus, chlorine and iodine in quantities very close to those which correspond to an equimolar mixture of initial complexes. From these data we arrived at the conclusion that $KPCl_6$ is contained in the reaction product in only very negligible quantity, due to its solvolysis with iodine chloride according to Equation (1).

Gutmann [6] also failed to obtain positive results in analogous experiments with tetramethylammonium chloride. Conductometric titration of $(CH_3)_4NCl$ solution with a PCl_5 solution in phosphorus oxychloride did not indicate chemical reaction. Upon interaction of solutions of $(CH_3)_4NCl \cdot ICl$ and $PCl_5 \cdot ICl$ in iodine chloride we obtained a bright-orange product, for which Gutmann, on the basis of results of quantitative determination of iodine and chlorine, chose the composition and structure $[(CH_3)_4N][PCl_6]ICl$.*

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* It may also be supposed that this product is a mixture of $(CH_3)_4NCl$ and $PCl_5 \cdot ICl$.

Finally, we must also note the work [10] in which upon reaction of PCl_5 and pyridine we obtained a crystalline substance $2C_5H_5N \cdot HCl \cdot PCl_5$, the structure of which by analogy with $SbCl_6H \cdot 2C_5H_5N$ [11] is given in the form $PCl_6H \cdot 2C_5H_5N$.

Proof of the existence of PCl_6^- ions in solutions is to be found only in the work of Payne [12], in which on the basis of electrolysis experiments on PCl_5 solutions carried out in acetonitrile and nitrobenzene, he postulates that the electrolytic dissociation of PCl_5 in these solutions takes place according to the scheme:

$$2PCl_5 \rightleftarrows PCl_4^+ + PCl_6^-. \tag{2}$$

Payne expresses the electrode processes as follows

$$PCl_6^- - e \rightarrow [PCl_6] \rightarrow PCl_5 + \frac{1}{2}Cl_2, \tag{3}$$

$$2PCl_4^+ + 2e \rightarrow [2PCl_4] \rightarrow PCl_3 + PCl_5. \tag{4}$$

The detection of phosphorous acid in the catholyte and free chlorine in the anolyte confirms these schemes.

Thus, the literature data indicate the relatively slight stability of hexachlorophosphates in the solid state. This, however, does not preclude the possibility of their formation in solutions due to the stabilizing action of the solvent. Therefore, we made a study of the systems PCl_5-HCl-solvent (nitrobenzene, acetonitrile) by methods of physicochemical analysis and ion transfer.

EXPERIMENTAL

The preparation of phosphorus pentachloride and the purification of the solvents were described previously [1, 13]. Solutions of hydrogen chloride in nitrobenzene and acetonitrile were prepared as follows: hydrogen chloride, prepared by the reaction of H_2SO_4 and NaCl, was passed through wash bottles containing water and (for dehydration) concentrated sulfuric acid. Then the organic solvent was saturated with dry HCl under conditions which excluded access of moisture. The prepared solutions were kept in sealed ampoules. Their HCl concentrations were determined by titration (Volhard).

In those cases when the investigation was carried out by the method of isomolar concentrations the PCl_5 solution was prepared in the same solvent and at the same concentration as the hydrogen chloride solution. The rest of the procedure was the same as in study of $PCl_5-AlCl_3(FeCl_3)-$solvent systems [1, 13].

When solutions with a constant molar ratio of HCl to solvent were subjected to investigation (in the study of the electrical conductivity of the systems), to a solution of HCl of known concentration weighed samples of PCl_5 were added, and after their complete solution and on keeping in a thermostat at a temperature of experiment of 25 and 45° (± 0.05°), the electrical conductivity of the system was measured.

The isotherms of specific conductivity of the system $HCl-PCl_5-$nitrobenzene (Fig. 1) take the form of straight lines. This dependence of the conductivity of the given system on concentration indicates, in particular, the absence of any complex-formation process between HCl and PCl_5 in the nitrobenzene solution.

Different results were obtained upon investigation of the system $HCl-PCl_5$ in acetonitrile; the isotherms of specific conductivity of the acetonitrile solutions have either a sharp curvature (in experiments with a constant molar ratio of HCl to CH_3CN, Fig. 2) or a maximum (in experiments with solutions of isomolar concentration, Table 1, Fig. 3), which correspond to an equimolar ratio of HCl and PCl_5 (at a molar ratio of HCl to CH_3CN = 1: ~40).

The results of measuring the conductivity of the system $HCl-PCl_5-CH_3CN$ give grounds for concluding that phosphorus pentachloride and hydrogen chloride react with each other in acetonitrile to form a compound of equimolar composition, $HCl \cdot PCl_5$, which has the character of a rather strong electrolyte; the specific conductivity of a 0.14 M solution at 25 and 45° is of the order of 10^{-3} - 10^{-2} ohm^{-1} cm^{-1}.

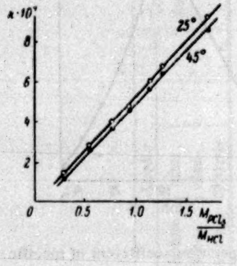

Figure 1. Specific conductivity of system $HCl-PCl_5-C_6H_5NO_2$. $M_{HCl}:M_{C_6H_5NO_2} = 1:43.9$.

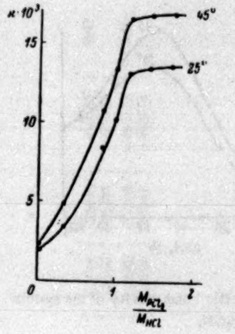

Figure 2. Specific conductivity of system $HCl-PCl_5-CH_3CN$. $M_{HCl}:M_{CH_3CN} = 1.0:39.5$.

TABLE 1

Specific Conductivity and Viscosity of System $HCl-PCl_5-CH_3CN$ ($C_{PCl_5} + C_{HCl} = 0.28$ M.)

Mole % PCl_5*	Specific conductivity $\kappa \cdot 10^3$ (ohm^{-1}cm^{-1})		Viscosity		Corrected specific conductivity $\kappa\eta \cdot 10^3$	
	25°	45°	25°	45°	25°	45°
0	1.46	1.72	—	—	—	—
10	2.16	2.80	0.435	0.357	0.94	1.00
20	3.65	4.74	0.443	0.367	1.62	1.74
30	5.29	6.64	0.451	0.378	2.38	2.51
40	6.86	8.54	0.443	0.365	3.05	3.11
50	7.48	9.43	0.435	0.353	3.25	3.33
60	7.39	8.86	0.439	0.355	3.24	3.15
70	6.73	7.57	0.442	0.361	2.97	2.73
80	5.71	6.25	0.452	0.367	2.58	2.29
90	4.95	5.15	0.460	0.373	2.28	1.92
100	4.56	4.45	—	—		

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* With respect to sum of both chlorides.

The formation of this compound is corroborated also by the fact that the temperature coefficient curve of the specific conductivity [14] has a sharp maximum that corresponds to the ratio $HCl:PCl_5 = 1$ (Fig. 4).

Measurement of the viscosity of the system $HCl-PCl_5-CH_3CN$, carried out in a viscosimeter, was used for work with non-aqueous solutions [15] and showed (Table 1) that with increase of the concentration of phosphorus pentachloride the viscosity of the system at first increases, reaching the value $\eta_{25°} = 0.451$ centipoise at 30 molar % PCl_5, then dropping to a value of 0.435 at 50% PCl_5; upon further addition of phosphorus pentachloride, it again increases. However, the change of viscosity in this system is relatively small, so that on the basis of its concentration dependence it could be possible to conclude that the extreme points found correspond to the formation of a compound of a particular composition.

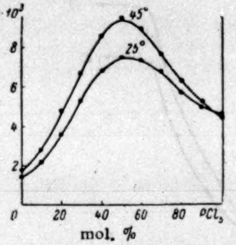

Figure 3. Specific conductivity of the system $HCl-PCl_5-CH_3CN$.
$C_{PCl_5} + C_{HCl} = 0.28$ M.

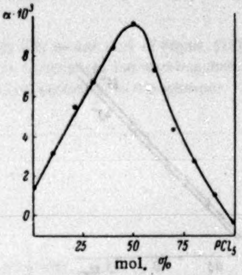

Figure 4. Temperature coefficient of specific conductivity of the system $HCl-PCl_5-CH_3CN$.
$C_{HCl} + C_{PCl_5} = 0.28$ M.

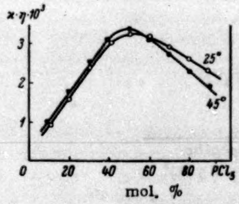

Figure 5. Specific conductivity, corrected for viscosity, of the system $HCl-PCl_5-CH_3CN$.
$C_{HCl} + C_{PCl_5} = 0.28$ M.

The results of measuring the viscosity of the system $HCl-PCl_5-CH_3CN$ were used for introducing corrections for viscosity into the magnitudes of the specific conductivity. In this case also the maximum of the corrected conductivity (Table 1, Fig. 5) corresponds to the concentration region that corresponds to the formation of a compound of equimolar composition, $HCl \cdot PCl_5$.

To clarify the nature of the ions in the acetonitrile solution of the system $HCl-PCl_5$ we carried out experiments on the study of ion migration. For electrolysis we used solutions with an equimolar ratio of hydrogen chloride to phosphorus pentachloride calculated on a content of 0.2-0.25 M of the compound $HCl \cdot PCl_5$. The prepared solutions were light-yellow in color.

Simultaneously, under analogous conditions we carried out experiments on ion migration in acetonitrile solutions of phosphorus pentachloride. The electrodes used were of silver, covered with a layer of silver chloride. The experiments were carried out at 25°. After electrolysis, the anodic, central and cathodic portions of the solution were analyzed for chlorine and phosphorus content. Chlorine was determined according to Volhard, and phosphorus was determined by titration of ammonium phosphomolybdate with caustic soda solution (Table 2).

In the process of electrolysis of the system $HCl-PCl_5-CH_3CN$ the catholyte almost completely decolorized, while the color of the anolyte deepened, becoming dark-yellow, i.e., taking on the color of a solution of phosphorus pentachloride in acetonitrile. The data of Table 2, A show that the content of phosphorus and chlorine increases in the anodic portion and decreases in the cathodic portion. In the system PCl_5-CH_3CN, transfer of phosphorus and chlorine to the catholyte was noted (Table 2, B). The transport number of phosphorus in this system (0.40-0.41) coincided with that found previously [12]; it proved slightly higher than the transport number of phosphorus in the ternary system (0.35-0.36). For chlorine in both systems the transport numbers were found to be equal or somewhat higher than unity. • This fact serves to indicate that chlorine is carried in the composition of complex ions.

• Payne's article [12] makes no mention of the transport number of chlorine in the system PCl_5-CH_3CN.

TABLE 2

Results of Experiments on Ion Migration

Concentration of solution (wt. %)	Amount of copper deposited in coulometer (g)	Substance determined	Cathodic			Central			Anodic			Transport number
			before electrolysis	after electrolysis	Δ	before electrolysis	after electrolysis	Δ	before electrolysis	after electrolysis	Δ	
			A. System $HCl—PCl_5—CH_3CN$									
8.93	0.0335	P	0.0599	0.0491	−0.0108	0.0526	0.0530	+0.0004	0.0680	0.0792	+0.0112	0.35
		Cl	0.4104	0.3696	−0.0408	0.3602	0.3597	−0.0005	0.4664	0.5064	+0.0400	
10.00	0.0261	P	0.0673	0.0584	−0.0089	0.0459	0.0455	−0.0004	0.0674	0.0768	+0.0094	0.36
		Cl	0.4614	0.4309	−0.0305	0.3151	0.3144	−0.0007	0.4623	0.4923	+0.0310	
			B. System $PCl_5—CH_3CN$									
14.98	0.0256	P	0.1210	0.1309	+0.0099	—	—	—	0.1148	0.1043	−0.0105	0.41
		Cl	0.6925	0.7245	+0.0320	—	—	—	0.6550	0.6235	−0.0315	
14.55	0.0283	P	0.1294	0.1302	+0.0108	—	—	—	0.1320	0.1208	−0.0112	0.40
		Cl	0.7407	0.7726	+0.0319	—	—	—	0.7558	0.7245	−0.0313	

DISCUSSION OF RESULTS

Physicochemical analysis of the system $HCl-PCl_5$ in acetonitrile solution (conductivity measurement method) showed that a complex compound, $HCl \cdot PCl_5$, forms in it. The fact that in a nitrobenzene solution of the system $HCl-PCl_5$ measurement of the electrical conductivity failed to detect this compound may be due to the fact that in the system with acetonitrile the participation of the solvent favors the formation of the complex. This supposition about the possible participation of acetonitrile in forming a complex compound of hydrogen chloride with phosphorus pentachloride confirms works which showed that in systems with acids acetonitrile exhibits basic properties [16]. This must be the cause of the rather high conductivity of solutions of HCl in acetonitrile, of the order of 10^{-3} ohm^{-1} cm^{-1} for $C = 0.28$ M (Table 1).

Thus, it may be assumed that the complex which forms in the system $HCl-PCl_5-CH_3CN$ has, in reality, the composition $nCH_3CN \cdot HCl \cdot PCl_5$.

To judge the nature of the ions in the system $HCl-PCl_5-CH_3CN$, it must be compared on the one hand with PCl_5-AlCl_3 ($FeCl_3$)−solvent systems, for which the formation of complexes of the type $[PCl_4]^+ [MCl_4]^-$ [1-3] was demonstrated, and on the other hand with the system PCl_5−acetonitrile. As was noted above [12], phosphorus pentachloride in this system dissociates into the ions PCl_4^+ and PCl_6^- ; however, since Payne's experimental data are inadequate for determining the nature of the ions, we carried out electrolysis of PCl_5 solutions in acetonitrile, and detected (Table 2, B) an increase in the concentration of phosphorus and chlorine in the catholyte, 2.6 g-atoms of chlorine being transferred with each g-atom of chlorine. The latter may be explained as being due to the fact that in acetonitrile PCl_5 dissociates into PCl_4^+ and Cl^- ions.

However, neither Payne's experimental results nor ours can give a specific answer to the question of whether the dissociation of PCl_5 in acetonitrile follows the scheme $2PCl_5 \rightleftharpoons PCl_4^+ + PCl_6^-$ or the scheme $PCl_5 \rightleftharpoons PCl_4^+ + Cl^-$. *

Nevertheless, comparison of the phenomena that we detected during electrolysis of all these systems shows that the state of phosphorus pentachloride in the system $PCl_5-HCl-CH_3CN$ and its behavior during electrolysis are sharply different from its state and its behavior in systems with metallic chlorides or in acetonitrile solution: 1) while in the first of these systems as the result of electrolysis phosphorus is transferred to the anolyte (Table 2, A), in the other systems cited there is noted under analogous experimental conditions an increase in the concentration of phosphorus in the catholyte; 2) in the system $PCl_5-HCl-CH_3CN$ phosphorus pentachloride enters into the composition of the complex anion, since in this system chlorine also, evidently in the form of PCl_6^- ions, is transferred to the anode.

Quantitative data, given in Table 2, A, show that with each g-atom of phosphorus, a total of 2.9-3.1 g-atoms of chlorine is transferred to the anolyte. This may be explained by the fact that, due to the relatively slight stability of the complex $nCH_3CN \cdot HCl \cdot PCl_5$ and also to the presence in the system of its thermal dissociation products, side by side with electrolysis of the complex there may take place simultaneous electrolysis of PCl_5 in acetonitrile.

Thus, the results of the conductivity measurements and the experiments on ion migration in the system $PCl_5-HCl-CH_3CN$ lead to the conclusion that the complex compound of PCl_5 with hydrogen chloride which forms in this system dissociates into an anion PCl_6^- and a cation, which is a hydrogen ion solvated with acetonitrile.

The above-given data give grounds for expressing the composition of this complex and the products of its electrolytic dissociation by this scheme:

$$[(CH_3CN)_n H]PCl_6 \rightleftharpoons [(CH_3CN)_n H]^+ + PCl_6^- .$$

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* A more thorough study of this problem and clarification of whether during electrolysis there takes place simultaneous transfer of phosphorus to the catholyte and anolyte may be effected via a method employing labeled atoms.

Acetonitrile, by solvating the cation of the halogen acid, decreases the effect of counterpolarization and increases the stability of the complex anion.

SUMMARY

1. The method of conductivity measurements of the system PCl_5–HCl–acetonitrile was used to detect the compound of phosphorus pentachloride with hydrogen chloride of equimolar composition, which evidently also contains acetonitrile.

2. Study of the ion migration in the system PCl_5–HCl–CH_3CN showed that phosphorus and chlorine form the anion PCl_6^- of this complex compound, the structure of which may be represented by the formula $[(CH_3CN)_n H]^+ [PCl_6]^-$.

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CHANGE OF THE IONIC CONDUCTANCE OF LIQUID CHEMICAL COMPOUNDS AND SYSTEMS WITH TEMPERATURE

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The conductance of solutions, as a rule, has been studied at 18 and 25°, and only in isolated instances did the temperature interval in which this property was studied attain 50-100°; therefore, the change of ionic conductance (which we shall subsequently refer to as conductivity) with temperature remained outside the scope of most investigators.

Up to the present, the rise of conductivity with temperature has been considered to be as characteristic a feature of electrolyte as decrease in the magnitude of this property with rise of temperature is for metals. The negative temperature coefficient of conductivity, found for certain solutions, is considered to be more or less accidental, and has no valid explanation.

In the present article we consider the change of conductivity with temperature, and offer an equation which relates conductivity to temperature and other properties of the system. It is shown that by study of the theoretical and experimental material relating to conductivity at different temperatures we may conclude that the negative temperature coefficient of conductivity of electrolytes is not accidental, but has at least as large (if not larger) a region of relevance than the positive temperature coefficient of this property.

Aqueous solutions. F. Kohlrausch investigated the conductivity of aqueous solutions of a series of salts, acids and bases, and calculated the temperature coefficient of this property to be between 18 and 26°. The temperature coefficient of conductivity proved to be larger, the smaller the magnitude of the conductivity; it decreases somewhat with rise in temperature [1].

S. Arrhenius measured the equivalent conductivity of a number of aqueous solutions of salts and acids at 18 and 25°, and found that for copper sulfate and for acids the temperature coefficient decreased with rise of temperature. Arrhenius derived the equation of the polytherm of equivalent conductivity, from which it follows that it passes through a maximum, the existence of which was established for a 1.014 N solution of H_3PO_2 and a 2.94 N solution of H_3PO_4 [2].

G. Wegelius continued the measurements of Arrhenius on the conductivity of H_3PO_2 and H_3PO_4 at different temperatures, and found that with increase of the concentration of the acid the temperature of the molecular-conductivity maximum at first drops and, having reached a minimum for a 1 N solution of ~~H_3PO_2~~ at about 52° and for 1.96 N H_3PO_4 at 70°, it starts to rise with further increase of the concentration [3].

P. Sack found maxima on the conductivity polytherms of aqueous solutions of 0.321, 0.5 and 0.64% copper sulfate at 94°, 95° and 96°, respectively [4].

A. Noyes and associates obtained data on the equivalent conductivity of solutions of chlorides of sodium and potassium (0.5, 2.0, 10 and 100 mmole/liter) at 18, 100, 218, 281 and 306° and also for solutions of other salts and acids at elevated temperatures. With increase of the concentration of the solution the polytherms all diverge increasingly from a straight line, and a maximum appears on the polytherms of 0.1 N solutions of NaCl and KCl. The authors assert that for all, without exception, of the aqueous solutions of salts, acids and bases (chloride, acetate and hydroxide of sodium, nitrates of silver and barium, sulfate of magnesium, chloride and sulfate of potassium, hydroxide of barium, and hydrochloric, nitric, sulfuric and phosphoric acids) which they investigated, the degree of dissociation decreases with rise of temperature [5, 6].

Non-aqueous solutions. P. Walden and M. Centnerschwer found negative temperature coefficients of conductivity for solutions of ammonium thiocyanate and other substances in liquid sulfur dioxide. The temperature of the conductivity maximum on the polytherms rises with increase of the salt concentration [7]. Franklin and Kraus detected maxima on the conductivity polytherms of solutions of various salts in liquid ammonia [8]. A number of other examples of decrease in the conductivity of non-aqueous solutions with rise in temperature may be found in the monographs of P. Walden [9, 10].

Fused salts. In high conducting fused salts and systems composed of them, negative temperature coefficients are rarely encountered. Thus, for example, in the book of P. F. Antipin et al. [11], in which conductivity tables are given for a number of fused salts, it is possible to find data on the decrease of conductivity with rise of temperature only for two high conducting salts, namely for the trichloride and tribromide of indium; in systems of poorly conducting salts, for example, in solutions of the bromide of mercury (or antimony) and aluminum bromide the maximum on the conductivity polytherms was detected between 120 and 190°; for a solution of potassium bromide (high conducting in unadmixed liquid state) there was no maximum on the polytherms [12].

Theoretical and survey works devoted to the change of conductivity with temperature. Of the authors who studied experimentally the change of conductivity with temperature, Arrhenius [2], Wegelius [3] and Noyes [5, 6] explained the decrease in conductivity with rise of temperature by decrease in the degree of dissociation of the electrolyte. Bousfield and Lowry [13], who studied the conductivity of aqueous solutions of sodium hydroxide, postulated that the change in conductivity with rise in temperature was due, on one hand, to decrease in viscosity and, on the other hand, to decrease of the degree of dissociation. The temperature coefficient will be positive or negative depending on which of these effects predominates in the given temperature interval. If the effect of the decrease in viscosity is predominant, which takes place at normal temperatures, then the conductivity will rise with temperature; if the effect of the decrease in the degree of dissociation predominates, then the conductivity will fall. The conductivity polytherm of NaOH solutions at first rises, passes through a maximum (when both of the cited factors have an equal effect) and then falls.

F. Lindemann explained the fact, known since the time of Kohlrausch's works, of the more rapid increase in mobility of the slowest ions with rise of temperature, on the basis of the frequency of collision between ions of the electrolyte and the molecules of the solvent [14].

W. Biltz, in a paper devoted to the temperature coefficients of conductivity, shows that the magnitudes of these coefficients for all electrolytes depend, first of all, on the absolute value of the conductivity of the latter, independent of the nature of the substance. The temperature coefficients are smaller the better the conductivity [15].

R. Fuos shows that the temperature coefficient of weak electrolytes is a function of the ionic radius, the dielectric constant, the temperature, the concentration and the viscosity. By differentiation of the expression for this function he attempted to obtain the equation for the dependence of the change of conductivity with temperature on the change of the dielectric constant and the viscosity (or fluidity) for a constant concentration of electrolyte and a constant ionic radius [16].

M. Usanovich, differentiating the expression $\kappa = \frac{\sigma}{\eta}$, in which κ is the conductivity and η is the viscosity, arrives at the conclusion that the smaller the change of viscosity of the solution with temperature, the more readily a negative temperature coefficient of conductivity may appear [17].

P. Walden, in his monograph devoted to the conductivity of solutions [10], discusses the effect on the conductivity of increased in temperature, allowing for the changes of various factors with temperature separately for the solvent and solute. Upon raising the temperature, there is a decrease in the viscosity, the capacity for association, the van der Waals forces, the solvation forces and the permittivity of the solvent. Decrease in the first two factors and the solvation forces leads to increase in the conductivity with temperature, and decrease in the van der Waals forces and permittivity leads to its decrease.

Upon increase in the temperature, the following phenomena take place in the electrolyte solution: 1) the viscosity falls, and hence, the mobility of the ions increases; 2) the ionic volume decreases due to depolymerization, dehydration or cleavage of complex ions; 3) the complexity of the electrolyte molecules decreases and the dissociation scheme becomes more simple; 4) the degree of dissociation of the electrolyte decreases (due to the reaction heat of dissociation into ions). The first three factors lead to increase in the conductivity, the fourth factor acts in the reverse direction [10].

New theories of conductivity, based on data for extremely dilute solutions, almost disregard the problem of the change of conductivity with temperature. Thus, for example, in the long monograph of G. Falkengagen [18] only one page is devoted to the change in conductivity with temperature, which is illustrated by a figure taken from the work of Noyes [6], in which the equivalent conductivity isotherms of dilute solutions of sodium chloride are shown.

In his book, devoted to solutions, V. K. Semenchenko [19] discusses the problem of the change of conductivity with temperature as did Falkengagen, filling the corresponding place in his book (half a page) with the same illustration from Noyes' book.

Clarification of certain terms used in the theory of electrolytes. Study of the literature on the dependence of conductivity on temperature leads us to believe that the factors related to this dependence act either on all electrolytes, as, for example, the change in viscosity, or on separate groups of electrolytes, as, for example, the change of the degree of dissociation with temperature. The need therefore arises for classification of conducting compounds and systems into groups according to the nature of this basic property-conductivity.

It must be noted first of all that the basic term applied to conducting substances, namely "electrolyte", suffers from ambiguity, since this word is used at present in two senses: 1) electrolyte – a compound (i.e. chemical compound) which dissociates into ions and conducts a current; 2) electrolyte – any conductor of the second class, i.e., any systems or solutions which conduct current due to the presence of ions in them; in the first and in the second case the possibility of decomposition of the compounds by an electric current is implied.

Most of the definitions of the term "electrolyte" encountered the works of Faraday, who suggested this term, agree with the above-cited first meaning, but there is a definition that agrees also with the second meaning. The following passage in "Experimental Investigations on Electricity" agrees with the first definition. "Many substances are directly decomposed by an electric current, during which their elements are liberated" [20]. As for the definition that agrees with the second meaning, this passage is cited: "Those substances which when located between the metals of a voltaic cell, cause it to function are all electrolytes" [20].

We will adhere to a broader definition of the term "electrolyte", considering it to include not only conducting individual compounds but also conducting solutions and systems which are being discussed, as was stated in the beginning of this paper, on the basis of their ionic conductivity.

The presently accepted division of electrolytes into strong and weak electrolytes is based on the nature of the change of the molecular conductivity with concentration in the region of extreme dilutions, and is utterly inapplicable to the study of the conductivity of systems in a broad interval of concentrations, as may be illustrated by the following example. Aqueous solutions of both lithium chlorate and sulfuric anhydride are considered strong electrolytes. However, solutions of the first conduct current at low concentrations of the salt up to its pure melt, while solutions of the second conduct readily only in a certain interval of concentrations. Pure sulfuric anhydride virtually does not conduct current, and solutions which it quantitatively predominates do not come under the definition of a strong electrolyte.

Previously [21] it was shown that the magnitudes of the conductivity of the components and the compounds formed by them in the liquid state determine the character of the change of conductivity with concentration and temperature; therefore, the classification of electrolytes should be based on the conductivity values for individual liquid compounds and any composition of their solution. From this standpoint, the classification suggested by Bousfield and Lowry, after Armstrong, in which all electrolytes are divided into autolytes and heterolytes, appears quite useful [22]. Autolytes denote electrolytes that conduct in their individual liquid state; their solutions also conduct, unless they enter with the solvent into compounds that do not possess an ionic structure. Heterolytes refer to substances that do not conduct in their individual liquid state, but which with certain other substances give conducting solutions. To these substances belong, for example, anhydrides of oxygen acids and hydrogen halides that give conducting solutions with water.

W. Blum suggests the name ionogen for every chemical compound that is capable of forming ions upon being placed in a special medium, and the name electrolyte for every system or medium which may be decomposed upon passage of an electric current [23].

We will define an autolyte as a substance which conducts in the individual liquid state and a heterolyte as a conducting system, the components of which do not conduct in the individual liquid state. Since absolutely non-conducting substances do not exist, we will conditionally designate as conductors those substances (compounds and systems) the conductivity of which is greater than 10^{-5} ohm^{-1} cm^{-1} [21].

Properties of electrolytes that determine the change in conductivity with temperature. Of the phenomena that determine the change in conductivity with temperature, the degrees of dissociation and the permittivity are the most frequently encountered. Decrease in conductivity with temperature has been explained by the resultant decrease in the degree of dissociation of the electrolyte or in the permittivity [10]. However, such explanations are not soundly based, since, in most cases there is a lack of experimental data that might provide a basis for analysis of the change in the degree of dissociation or permittivity of electrolytes with temperature. In particular, we do not have sufficient grounds for assuming that the degree of dissociation of autolytes changes with change in temperature.

The change in viscosity and density which is observed in electrolytes with change in temperature [10] is undoubtedly associated with change in conductivity, but consideration of merely these two phenomena is still insufficient to explain the change in conductivity that takes place. In effect, with rise in temperature the viscosity always falls, due to which the conductivity should increase; however, this increase is less than the decrease in viscosity, and sometimes a decrease in conductivity is observed. Change in density with rise in temperature leads to decrease in the number of ions per unit volume, but upon introducing a correction for this circumstance (for example, by multiplying the conductivity by the specific volume, as for calculation of the so-called molecular conductivity), the respective polytherms still show maxima [6].

Thermal agitation of ions. One phenomenon is observed in electrolytes which, side by side with change in viscosity and density, determines the magnitude of their conductivities at different temperatures. We have in mind the effect of the thermal agitation of ions, ignored by almost all authors who work in this field.

It is known that all theories of metallic conductivity derive from consideration of the thermal agitation of ions and electrons of a metal, in which the decrease in conductivity observed in the metal with rise of temperature is explained by the increased intensity of this agitation, which leads to the increase in "interferences" on the path of the current-conducting electrons to the side opposite to the direction of the applied electric field [24].

It is quite evident that, despite the difference in the mechanism of the conductivity of metals and electrolytes, the thermal agitation of the ions of a liquid electrolyte increases its resistance. Intensification of the oscillations of molecules and ions about their temporary equilibrium positions and increase in the frequency of the collisions between these particles hinder the migration of ions in the direction of the lines of force of the external electric field. Although the theory of this problem has not as yet been given a detailed treatment, as a first approximation it may be assumed that the thermal agitation of the ions of an electrolyte decreases its conductivity proportional to its temperature, raised to some power n, which in its turn is a function of the temperature.

Thus, we consider three closely interrelated factors – the thermal agitation of ions, density (d) and viscosity (η), which in all cases, without exception, affect the change of conductivity with temperature. For autolytes these effects completely determine the change in conductivity with temperature, since the change in the electrostatic interaction between ions which takes place in this case is associated with the change in density that we considered.

Considering the change in conductivity to be under the influence of the thermal agitation of ions exclusively, and taking the density d and the viscosity η as constant, it may be assumed that the ratio of the magnitudes of κ_2 and κ_1 for any electrolyte at temperature T_2 and T_1 (representing temperatures on the absolute scale) is inversely proportional to the ratio of these temperatures raised to the corresponding power, i.e.

$$\left(\frac{\varkappa_2}{\varkappa_1}\right)_{d,\eta} = \frac{T_1^m}{T_2^n}, \qquad (1)$$

where n in the general case is greater than m when $T_2 > T_1$.

For a relatively narrow temperature range it may be assumed that m = n. Consequently, Equation (1) may be written in this form:

$$\left(\frac{\kappa_2}{\kappa_1}\right)_{d,\,\eta} = \frac{T_1^n}{T_2^n}. \tag{2}$$

For temperatures that are close to room temperatures or not exceeding a few hundred degrees, the magnitude of exponent n is nearly unity, since the intensity of the thermal agitation of molecules and ions is assumed proportional to the absolute temperature [14].

The dependence of the change in the magnitude of the conductivity on the change of density with temperature is associated with the fact that, for a constant degree of dissociation, the number of ions between the electrodes decreases, due to the decrease in density of the electrolyte upon rise of temperature; the thermal expansion of the measuring vessel may be disregarded in this, since it is small in comparison to the expansion of the electrolyte [25]. Therefore, upon heating the electrolyte from T_1 to T_2, other conditions staying the same, its conductivity decreases proportionally to the decrease in its density, i.e.,

$$\left(\frac{\kappa_2}{\kappa_1}\right)_{\eta,\,T} = \frac{d_2}{d_1}, \tag{3}$$

where d_2 and d_1 are the densities of the electrolyte at temperatures T_2 and T_1. Finally, assuming that the decrease in viscosity upon rise of temperature causes a corresponding increase in conductivity [10], and assuming the other conditions constant, we may write:

$$\left(\frac{\kappa_2}{\kappa_1}\right)_{d,\,T} = \frac{\eta_1}{\eta_2}. \tag{4}$$

where η_1 and η_2 are the viscosities of the electrolyte at temperatures T_1 and T_2. Simultaneously accounting for the effect of the change in thermal agitation, density and viscosity with change in temperature and assuming that

$$\frac{\kappa_2}{\kappa_1} = \left(\frac{\kappa_2}{\kappa_1}\right)_{d,\,\eta} \cdot \left(\frac{\kappa_2}{\kappa_1}\right)_{\eta,\,T} \cdot \left(\frac{\kappa_2}{\kappa_1}\right)_{d,\,T}, \tag{5}$$

the following equation may be derived from Equations (2) - (5):

$$\frac{\kappa_2}{\kappa_1} = \frac{T_1^n}{T_2^n}\,\frac{\eta_1 d_2}{\eta_2 d_1}. \tag{6}$$

Having determined the density and viscosity of the electrolyte at one temperature, T_1, from one of the formulas suggested by different authors [26, 27] we may calculate the viscosity and density at another temperature, and, inserting these values in Equation (6), we may calculate the value of κ_2 at temperature T_2:

$$\kappa_2 = \frac{\kappa_1 T_1^n \eta_1 d_2}{T_2^n \eta_2 d_1}. \qquad (7)$$

In the table this equation was verified for different electrolytes.

The compositions of the solutions given in the table are in percentages by weight, and relate to the first component of the system; the temperatures are given in degrees Celsius; η, $\underline{d}$ and κ represent the experimentally obtained values of viscosity (in centipoises), density (in g/ml), and specific conductivity (in $\text{ohm}^{-1} \cdot \text{cm}^{-1}$), respectively; κ_η is the conductivity calculated by the change in viscosity and density according to the equation:

$$\kappa_\eta = \frac{\kappa_1 \eta_1 d_2}{\eta_2 d_1}, \qquad (8)$$

κ_T and $\kappa_{T^{3/4}}$ are the conductivities calculated by Equation (7), at n = 1 or n = $^3/_4$, respectively; Δ_T is the relative difference in the percentages between the calculated and experimental values of the conductivity:

$$\Delta_T = \frac{\kappa_T - \kappa}{\kappa} \cdot 100. \qquad (9)$$

For n = $^3/_4$ in Equation (9) κ_T is replaced by $\kappa_{T^{3/4}}$.

The table also shows that when only the change in viscosity and density with change in temperature are considered, i.e. when the value κ_2 is calculated by Equation (8), in all cases excessively high data are obtained for it. Correct results for autolytes are obtained only upon taking in account the thermal agitation of ions, i.e. upon calculating κ_2 by Equation (7).

For the appearance of a negative temperature coefficient of conductivity, for which $\kappa_2 < \kappa_1$, it is necessary that in Equation (7), which may be written in the following form:

$$\kappa_2 = \kappa_1 \frac{\eta_1}{\eta_2} \cdot \frac{d_2}{d_1} \cdot \frac{T_1^n}{T_2^n} \qquad (10)$$

the product of the three fractional factors for κ_1 be less than unity. Since the second and third factors are proper fractions ($d_2 < d_1$ and $T_1 < T_2$) which themselves, as well as their product, approach unity upon decrease of the temperature interval $T_2 - T_1$, then in order to fulfill the above-cited condition it is necessary that the first of these factors, i.e. $\frac{\eta_1}{\eta_2}$, which is greater than unity, also approach unity.

$$\kappa_2 \leqslant \kappa_1, \quad \text{if} \quad \frac{\eta_1}{\eta_2} \leqslant \frac{1}{\dfrac{d_2 T_1^n}{d_1 T_2^n}}.$$

Change in viscosity at high temperatures. A study of the experimental data by viscosity polytherms and also the formulas suggested for their calculation [26, 27] leads us to conclude that these curves are similar in form to hyperbolas, each of which in a definite temperature region asymptotically approaches the temperature

Electrolyte (concentration, temperature)	η	d	$\varkappa$	$\varkappa_\eta$	$\varkappa_T$	$\varkappa_{T^{3/4}}$	Δ_T (%)	$\Delta_{T^{3/4}}$ (%)	Literature source
$AgClO_4$—H_2O (9.12%)									[28]
0°	1.765	1.0815	0.02684	—	—	—	—		
50°	0.560	1.0651	0.06937	0.07428	0.06853	0.069988	−1.21	0.74	
$LiNO_3$—CH_3OH (10.82%)									[29]
0°	2.074	0.9271	0.01766	—	—	—	—	—	
50°	0.834	0.8620	0.0350	0.04084	0.03451	0.03600	−1.40	2.85	
$NaNO_3$									[31]
325°	2.75	1.899	1.072	—	—	—	—	—	
450°	1.55	1.807	1.587	1.810	1.497	1.570	−5.67	−1.07	
$CaCl_2$—NaCl (65.5%)									[31]
700°	3.95	1.855	1.811	—	—	—	—	—	
825°	2.80	1.808	2.256	2.490	2.207	2.274	−2.12	0.80	
HCl—H_2O (30.01%)									[30]
−30°	5.705	1.1752	0.2461	—	—	—	—	—	
0°	2.557	1.1600	0.4909	0.5547	0.4825	0.4969	−1.71	1.22	
25°	1.588	1.1459	0.7299	0.7807	0.7152	0.7328	−2.01	0.51	
$HClO_4$—H_2O (49.88%)									[30]
−30°	8.435	1.4130	0.1886	—	—	—	—	—	
0°	2.863	1.3870	0.4238	0.5557	0.4845	0.5090	14.30	20.10	
25°	1.625	1.3637	0.6457	0.7393	0.6773	0.6939	4.90	7.46	
SO_3—H_2O (41.18%)									[32]
−23.6°	16.014	1.4304	0.1771	—	—	—	—	—	
15°	4.398	1.4019	0.5066	0.6312	0.5465	0.5666	7.88	11.84	
H_3PO_4—H_2O (42.78%)									[33]
0°	7.906	1.2877	0.1429	—	—	—	—	—	
25°	3.631	1.2760	0.2287	0.3082	0.2822	0.2893	23.40	36.40	
50°	2.075	1.2619	0.3010	0.3955	0.3652	0.3757	21.30	24.80	

axis. On this portion of the polytherm the difference between the viscosity values for two temperatures, which are tens of degrees apart, is very small; the ratio $\frac{\eta_1}{\eta_2}$ may approach unity; and the fall of viscosity with temperature has no appreciable effect on the change of the conductivity. Therefore, in the temperature region of slow decrease in viscosity, for the given electrolyte the decrease in conductivity due to increase in the thermal agitation of ions with temperature becomes superimposed over the increase of conductivity due to the decrease in viscosity, and as a whole the magnitude of the conductivity falls with increase in temperature.

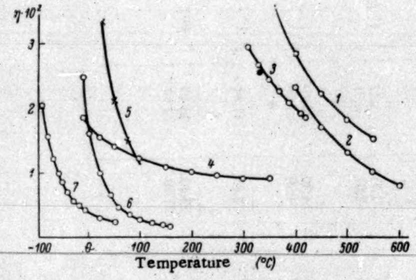

Figure 1. Viscosity polytherms of certain substances and solutions.
1) NaOH, 2) KOH, 3) $NaNO_3$, 4) Hg, 5) $LiClO_3$ (46.36%), 6) H_2O, 7) CH_3COCH_3.

At low temperatures and room temperatures the intensity of the thermal agitation is small, the decrease in the viscosity is considerable, and the conductivity increases with temperature.

From Fig. 1, where the viscosity polytherms of the pure substances are given according to [34] and that of an aqueous solution of $LiClO_3$ according to [35], it is apparent that there are three sections to the water polytherm. On the first of these, in the region between −10° and +20°, the curve sharply falls with increase in temperature; in the second, from 20° to 80-90°, the fall slows down; and, finally, in the third, above 80-90°, the curve slopes very gently – the change of viscosity with temperature is negligible. These three sections are theoretically possible for each curve, but are realized only where the substance exists in the liquid state under the experimental conditions. Thus, for example, for mercury the second and third sections are realized; evidently, the first lies in the region of supercooling. For the aqueous solution of $LiClO_3$ and for fused NaOH and KOH the first and second sections are realized (Fig. 1). Evidently, continuation of research in the field of higher temperatures will lead to the discovery of still a third section on these polytherms. It is apparent from Fig. 1 that for different substances and solutions the same sections of the polytherms lie in different temperature regions. In particular, for aqueous solutions the third section of the polytherm, in which viscosity slowly falls with rise in temperature, lies at a higher temperature the greater the concentration of the solution and, consequently, the higher the viscosity.

Non-aqueous solvents and solutions in them possess a lower viscosity than water and aqueous solutions. It is apparent from Fig. 1 that each of the three sections on the polytherm of acetone lies at a lower temperature than on the polytherm of water.

It is evident from inspection of the viscosity polytherms for fused NaOH, $NaNO_3$ and KOH that these curves have the same form as the polytherms of water, acetone and an aqueous solution of lithium chlorate. For the present we have obtained the upper portion of the polytherm for $NaNO_3$ and the middle portion for KOH and NaOH. It is certain, however, that measurements at higher temperature regions will result in the discovery of a third section on the viscosity polytherm, on which a retardation of the fall of viscosity with rise in temperature will be observed. It may be assumed that for fused hydroxides of potassium and sodium this will take place at 800-1000°.

It is evident from Fig. 2, which shows the conductivity polytherms for fused NaOH and KNO_3 [36] and for $NaNO_3$ [31], that these curves show a somewhat retarded rise with temperature in approximately those regions in which there is a marked retardation of the fall of viscosity on Fig. 1.

Difference in the change of conductivity of autolytes and heterolytes with change of temperature. It is apparent from the table that for autolytes and their solutions (fused $NaNO_3$ and the system $CaCl_2-NaCl$ and also $AgClO_4$ solution) it is possible to calculate the value of κ_2 by Equation (7) with sufficient accuracy. A solution of $LiNO_3$ and CH_3OH possesses a relatively low conductivity and, evidently, the degree of dissociation of this electrolyte decreases somewhat with temperature, since at $n = ^3/_4$ calculation give a value for κ_2 which is 2.85% greater than that found experimentally. Sodium nitrate and a mixture of calcium and sodium chlorides in the molten state, evidently, completely break up into ions in the temperature range given in the table, since the calculated value of κ_2 is not greater than that found experimentally.

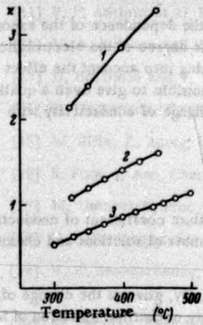

Figure 2. Conductivity polytherms for fused salts. 1) NaOH, 2) $NaNO_3$, 3) KNO_3.

Aqueous solutions of perchloric and sulfuric acids evidently decrease the degree of their electrolytic dissociation (or, which is more probable, increase the degree of thermal decomposition of the conducting complex) with rise in temperature, since the calculated κ_2 is greater than the experimentally found value.

The theory of physicochemical analysis states that it is necessary to study the properties of systems in broad intervals of change in the conditions that determine the state of a system – concentration, temperature and pressure [37, 38]. Neglect of these axioms has led to conclusions that are often of limited application and sometimes prove incorrect in principle upon examination of the change in the property in a broad range of concentrations and temperatures. This is precisely the case with the change of conductivity with temperature. A positive temperature coefficient of this property was considered to be as characteristic for electrolytes as was a negative temperature coefficient for metals. However, after experimental finding of cases in which the conductivity of electrolytes decreases with rise in temperature, such an assumption can no longer be considered correct. As shown above, upon broadening the temperature interval of measurements toward higher temperatures, we invariably reach a region of negative temperature coefficients of conductivity. It follows from this that a positive temperature coefficient is only a particular case occurring in a definite temperature region in which the viscosity is relatively high and falls rapidly with rise in temperature. Thus, a negative temperature coefficient is not at all accidental for electrolytic conductivity; it must occur for each chemical compound or solution if they can maintain their liquid state at a sufficiently high temperature.

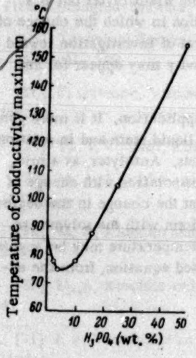

Figure 3. Change of temperature of the conductivity maximum with variation of concentration on the conductivity polytherms of system phosphoric acid-water.

Upon increasing the concentration of the conducting compound, the temperature of the maximum on the conductivity polytherms at first falls somewhat, as in the dilute solutions studied by Noyes [5, 6], and then begins to rise, as may be seen from the data obtained by the author jointly with M. Sh. Kurbanov in the investigation of conductivity and viscosity in the system phosphoric acid–water [33].

It is evident from Fig. 3 that the temperature of the conductivity maximum at first falls with increase in concentration, reaching a minimum at 5 mole % acid and 65°, and then begins to rise almost linearly with temperature.

Besides the change in viscosity, density and intensity of the thermal agitation with rise in temperature that occurs for autolytes as well as heterolytes, the latter may also undergo thermal decomposition of the current-conducting compound, which results in lowering of the temperature at which a negative temperature coefficient of conductivity appears. This, in reality, is observed for acids, which show a rapid fall in conductivity with rise in temperature. The same phenomenon occurs in many non-aqueous systems, for which the importance of viscosity is relatively great in this respect.

In readily-conducting fused salts and their systems a negative temperature coefficient may appear, depending on the nature of the change of viscosity with change in temperature over an interval of 400° and more from the temperature of transition from the solid to the liquid state.

Development of the theory of conductivity will lead to clarification of the dependence of the exponent in Equation (7) on temperature, after which it will be possible to determine the degree of the electrolytic and thermal dissociations that are not accounted for by this equation. Without taking into account the effect of the thermal agitation of ions, side by side with density and viscosity, it is impossible to give even a qualitatively correct representation of the role of other factors that condition the change of conductivity with temperature.

SUMMARY

1. Increase of conductivity with temperature, i.e., the positive temperature coefficient of conductivity, does not always take place in liquid electrolytes and their solutions. For a number of solutions and chemical compounds negative temperature coefficients of conductivity were found.

2. The most important factor which, side by side with viscosity and density, governs the change of conductivity of all liquid electrolytes, without exception, is change in the intensity of thermal agitation of ions. Increase in the intensity of thermal agitation of ions with rise in temperature decreases the conductivity of the electrolyte, due to hindrance of the migration of ions in the direction of the electrodes.

3. An equation has been put forth by means of which it is possible to calculate the conductivity of the electrolyte at a certain temperature, using the viscosity and density values for two temperatures and the value of the conductivity for one temperature.

4. A negative temperature coefficient of conductivity is not an accident for electrolytes but is a characteristic feature. It appears in those regions of temperature and concentration in which the change of viscosity with temperature is not great. Upon broadening the temperature interval of investigation toward the direction of higher temperatures, a negative temperature coefficient of conductivity may appear for any electrolytes and, in particular, in salt melts.

5. The separation of electrolytes into "strong" and "weak" is of limited application. It is more general and acceptable to divide them into autolytes, conducting both in the individual liquid state and in solutions, and heterolytes, which form conducting solutions from non-conducting components. Autolytes, as a rule, completely dissociate into ions, or, in any case, do not change their degree of dissociation with change of concentration and temperature; for heterolytes it is necessary to take into account the change in the degree of electrolytic or thermal dissociation of the conducting compounds which they form with the solvent (or other component of the system). The change in the degree of dissociation with temperature may be approximately calculated by the deviation of the conductivity calculated by the suggested equation, from the experimentally found value.

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VAPOR PRESSURE OF THE SYSTEMS $NaCl - CaCl_2 - H_2O$ and $KCl - CaCl_2 - H_2O$

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As a method of physicochemical analysis, tensimetry has been little used for the study of processes that take place in aqueous salt solutions. In particular, the dependence of the vapor pressure of mixed solutions of salts on their composition (even for the simplest systems in which there is no complex-formation) has been little studied up to the present. The vapor pressure of two ternary systems was studied in the present work.

The solubility data [1] show that in solutions which contain sodium and calcium chlorides no double salt is formed. Chemical interaction is also absent in melts of these salts [2]. In the system $KCl-CaCl_2$ complex-formation was detected by recording curves of fusion, conductivity and molecular volume [2]. In presence of water these salts form a compound of the composition $KCl-CaCl_2$ in the solid phase [1].

The cited systems were investigated in order to establish the character of the dependence of the vapor pressure of mixed solutions on their composition.

EXPERIMENTAL

Procedure. Chemically pure sodium chloride and potassium chloride were twice recrystallized and dried at 120° to constant weight. Chemically pure calcium chloride was also purified by recrystallization from water and was used in the form of the crystal hydrate, $CaCl_2 \cdot 6H_2O$.

The ternary systems were studied in sections corresponding to a constant sum of the salts. For this, initial solutions of each salt of the same molecular concentration were preliminarily prepared. The composition of the solution of calcium chloride was established via Ca and Cl, and was regulated by the specific gravity. Before each measurement the initial solutions were mixed in the given ratios.

A dynamic method was used for measuring the vapor pressure. The main part of the apparatus that served for this purpose was an ebullioscope of about 250 ml capacity, with double walls between which the thermostat liquid circulated. Internal heating was carried out by means of a nichrome spiral situated in a test tube with glycerin that was attached to the casing. 100 ml of the investigated solution was placed in the ebullioscope, and in order to assure even boiling about 10-15 capillaries were added. The boiling point was registered by a checked thermometer with 0.1° divisions and a correction for the projecting column of the thermometer.

The vapor pressure values were found from the expression:

$$P = P_{atm.} - \Delta P$$

in which: P is the vapor pressure of water over the solution (mm Hg); $P_{atm.}$ is the atmospheric pressure, referred to 0°; ΔP is the difference in the readings of the right and left bends of the manometer, with corrections for temperature.

To test the tensimeter, experiments were carried out to determine the vapor pressure of water at several temperatures and the obtained data were compared with the literature data.

System $NaCl-CaCl_2-H_2O$. The vapor pressure of the given system (one section corresponding to a sum of 7.86 mole % salts) was studied in the temperature interval approximately from 70-85°. The obtained results are given in Table 1.

TABLE 1

Vapor Pressure of the System $NaCl-CaCl_2-H_2O$
(Isoconcentrate 92.14 mole % H_2O)

Molecular percentages of total salt content in system		Tem-perature	Vapor pressure (mm Hg)	Molecular percentages of total salt content in system		Tem-perature	Vapor pressure (mm. Hg)
$CaCl_2$	NaCl			$CaCl_2$	NaCl		
0.00	100.00	69.8°	189.2	55.13	44.87	70.9	167.6
0.00	100.00	71.9	207.3	55.13	44.87	72.9	182.5
0.00	100.00	74.2	229.6	55.13	44.87	75.5	204.4
0.00	100.00	76.8	256.0	55.13	44.87	78.8	234.2
0.00	100.00	79.9	290.1	55.13	44.87	80.6	251.9
0.00	100.00	81.8	311.1	55.13	44.87	82.5	270.1
0.00	100.00	84.0	337.1	55.13	44.87	84.2	289.7
0.00	100.00	85.6	362.1	55.13	44.87	85.3	302.3
17.39	82.61	69.6	178.5	63.87	36.13	69.6	153.2
17.39	82.61	72.1	199.1	63.87	36.13	71.3	165.3
17.39	82.61	74.0	215.3	63.87	36.13	73.2	179.9
17.39	82.61	76.9	244.3	63.87	36.13	75.0	194.4
17.39	82.61	79.6	272.8	63.87	36.13	77.4	214.8
17.39	82.61	82.1	298.9	63.87	36.13	79.9	238.9
17.39	82.61	84.4	328.3	63.87	36.13	82.3	262.1
17.39	82.61	85.6	344.1	63.87	36.13	84.4	287.0
29.88	70.12	68.7	162.8	63.87	36.13	85.1	295.1
29.88	70.12	71.3	184.6	76.69	23.31	69.3	143.8
29.88	70.12	72.7	195.7	76.69	23.31	70.9	153.6
29.88	70.12	74.2	206.9	76.69	23.31	73.3	169.6
29.88	70.42	76.5	232.0	76.69	23.31	74.8	180.3
29.88	70.12	77.8	242.0	76.69	23.31	77.4	202.6
29.88	70.12	80.1	267.5	76.69	23.31	79.8	224.1
29.88	70.12	82.9	298.5	76.69	23.31	82.1	247.1
29.88	70.12	85.2	227.3	76.69	23.31	83.4	259.9
46.22	53.78	68.9	159.0	76.69	23.31	85.2	276.2
46.22	53.78	71.1	174.0	100.00	0.00	68.8	126.5
46.22	53.78	72.9	188.1	100.00	0.00	71.1	139.3
46.22	53.78	75.9	213.9	100.00	0.00	73.0	152.5
46.22	53.78	79.0	243.6	100.00	0.00	75.2	167.0
46.22	53.78	82.1	275.2	100.00	0.00	78.3	189.5
46.22	53.78	83.7	293.6	100.00	0.00	81.1	212.2
46.22	53.78	85.3	313.0	100.00	0.00	84.2	241.2
55.13	44.87	69.3	157.5	100.00	0.00	85.4	253.3

The data of Table 1 are shown graphically in Fig. 1. The temperature dependence of the vapor pressure of solutions of sodium chloride (upper curve), calcium chloride and their mixtures is represented by curves which show convexity toward the temperature axis. The decrease in the vapor pressure over the $CaCl_2$ solution is considerably greater than over the sodium chloride solution.

Figure 2 shows vapor pressure isotherms in the section of the system $NaCl-CaCl_2-H_2O$. The 55 and 65° isotherms were plotted by interpolation of the curves of Fig. 1. Figure 2 shows the character of the change in vapor pressure upon mixing solutions of sodium and calcium chlorides of the same concentration. This dependence is virtually a linear function of the molar ratios of the electrolytes of the system, although the initial, relatively concentrated solutions differ markedly in the magnitude of this property. (Analogous results were obtained in study of the system $Na_2S-Na_2SO_4-H_2O$.)

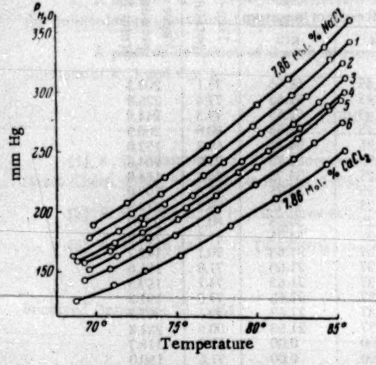

Figure 1. Dependence of vapor pressure of system $NaCl-CaCl_2-H_2O$ on temperature (sum of salts 7.86 mole %).
1) 82.61% NaCl, 2) 70.12% NaCl, 3) 53.78% NaCl, 4) 44.87% NaCl, 5) 36.13% NaCl, 6) 23.31% NaCl (percentages are of the total salts).

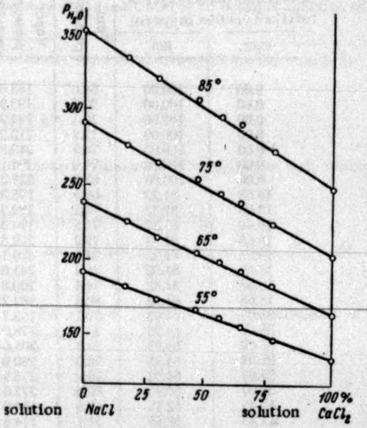

Figure 2. Vapor pressure isotherms of systems $NaCl-CaCl_2-H_2O$ in section corresponding to 92.14 mole % water.

For the simplest systems it should be possible to expect deviation of the vapor pressure from the vapor pressure of an ideal system if the ions of the electrolytes differ markedly among themselves in their relationship to water. Under this condition mixing of concentrated solutions of individual salts may lead to some redistribution of water molecules between unlike ions, due to their competition for possession of the solvent. However, these processes, evidently, are weakly expressed in aqueous solutions containing $CaCl_2$ and NaCl, and are therefore not reflected on the vapor-pressure diagram; the isoconcentrate isotherms are linear.

System $KCl-CaCl_2-H_2O$ was studied in one section corresponding to 91.23 mole % water in a temperature interval approximately from 70-80°. The results of the vapor pressure measurements are given in Table 2.

The tensimetric data are given in the form of a graph showing the dependence of the vapor pressure of water over solutions of potassium chloride, calcium chloride and their mixtures on the temperature (Fig. 3).

The 70, 75 and 80° isotherms, shown in Fig. 4 quite convincingly show the increase in vapor pressure relative to the additive magnitude (the deviations reach the order of 4%). With the example of the system $KCl-MgCl_2-H_2O$ [3] we previously showed that positive deviations of the vapor pressure from the additive line (in the study of diagonal sections) are due to the formation of complex ions.

On comparing the obtained results, it must be noted that there is a qualitative difference between the systems $NaCl-CaCl_2-H_2O$ and $KCl-CaCl_2-H_2O$: the isoconcentrate isotherms of the vapor pressure of the first system are linear, while upon mixing of solutions of KCl and $CaCl_2$ a positive deviation of this property from a linear dependence is observed. Here there is evidence of difference in the behavior of Na^+ and K^+ ions in solution, which is evidently due to the different energy characteristics of these ions.

TABLE 2

Vapor Pressure of the System $KCl-CaCl_2-H_2O$
(Isoconcentrate 91.23 mole % H_2O)

Molecular percentages of total salt content in system		Temperature	Vapor pressure (mm Hg)	Molecular percentages of total salt content in system		Temperature	Vapor pressure (mm Hg)
$CaCl_2$	KCl			$CaCl_2$	KCl		
0.00	100.00	69.0°	183.0	47.45	52.55	75.1°	207.3
0.00	100.00	70.2	193.9	47.45	52.55	77.4	226.8
0.00	100.00	70.4	194.9	47.45	52.55	79.3	244.5
0.00	100.00	72.2	212.9	47.45	52.55	80.8	260.9
0.00	100.00	74.9	240.8	65.25	34.75	69.2	152.0
0.00	100.00	79.8	294.1	65.25	34.75	71.2	164.6
0.00	100.00	82.5	325.2	65.25	34.75	74.0	184.0
18.68	81.32	68 8	175.0	65.25	34.75	75.8	199.0
18.68	81.32	70.1	183.9	65.25	34.75	78.2	217.8
18.68	81.32	71.5	194.3	65.25	34.75	80.3	237.9
18.68	81.32	73.2	209.8	65.25	34.75	81.5	248.3
18.68	81.32	74.9	226.1	78.37	21.63	70.1	142.7
18.68	81.32	76.4	241.0	78.37	21.63	71.8	151.6
18.68	81.32	78.4	260.8	78.37	21.63	74.1	169.3
18.68	81.32	80.4	282.2	78.37	21.63	77.2	191.2
35.07	64.93	69.1	168.3	78.37	21.63	79.1	207.7
35.07	64.93	70.3	178.0	78.37	21.63	80.6	221.8
35.07	64.93	73.7	205.6	100.00	0.00	69.8	118.7
35.07	64.93	76.3	230.0	100.00	0.00	71.6	130.0
35.07	64.93	78.9	255.9	100.00	0.00	74.0	145.0
35.07	64.93	80.6	273.6	100.00	0.00	76.9	163.6
47.45	52.55	69.5	164.0	100.00	0.00	78.6	178.2
47.45	52.55	71.1	174.6	100.00	0.00	80.4	192.1
47.45	52.55	73.2	190.8				

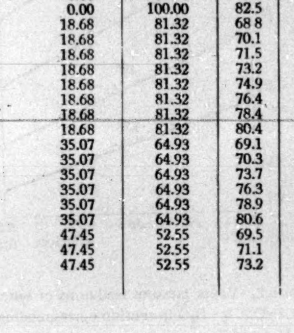

Figure 3. Dependence of vapor pressure of the system $KCl-CaCl_2-H_2O$ on temperature (total salts 8.77 mole %).
1) 81.32% KCl, 2) 64.93% KCl, 3) 52.55% KCl, 4) 34.75% KCl, 5) 21.63% KCl (percentages are of the total salts).

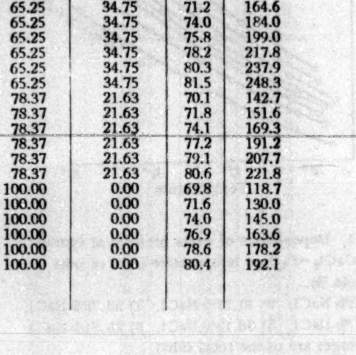

Figure 4. Vapor pressure isotherms of the system $KCl-CaCl_2-H_2O$ in section corresponding to 91.23 mole % water.

SUMMARY

1. The vapor pressure of solutions in sections of the ternary systems $NaCl-CaCl_2-H_2O$ (70-85°) and $KCl-CaCl_2-H_2O$ (70-80°) has been studied.

2. It is shown that the vapor pressure of mixed solutions of NaCl and $CaCl_2$ is an additive function of the molecular composition of the salts.

3. A positive deviation of the vapor pressure from additivity was established upon mixing equimolar solutions of KCl and $CaCl_2$.

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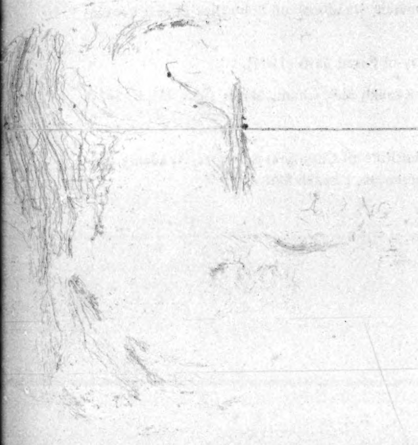

SOLUBILITY OF THE OXALATES OF CALCIUM, STRONTIUM, BARIUM, CADMIUM, COPPER AND LEAD IN AQUEOUS SOLUTIONS OF POTASSIUM NITRATE

M. P. Babkin

The slight solubility in water of the oxalates of a number of cations is widely used for their analytical determination by gravimetric and volumetric methods. However, the magnitude of the solubility of the precipitates in aqueous solutions is affected by presence in the solution of electrolytes with ions similar to and different from those of the precipitate.

TABLE 1

Solubility of Barium, Strontium and Calcium Oxalates in Aqueous Solutions of Ammonium Chloride

NH_4Cl M.	Solubility (mole/liter)		
	BaC_2O_4	SrC_2O_4	CaC_2O_4
0.025	$8.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	—
0.033	—	6.0	—
0.1	—	—	$10.7 \cdot 10^{-5}$
0.5	—	—	$23.0 \cdot 10^{-5}$
1.0	—	—	$28.0 \cdot 10^{-5}$
0.0	$4 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$

The solubility of precipitates of calcium, strontium and barium oxalates in aqueous solutions of ammonium chloride was studied by N. A. Tananaev and Kh. N. Pochinok [1, 2] and Kh. N. Pochinok [3], who established that even in slight concentrations ammonium chloride increases the solubility of calcium, strontium and barium oxalates several-fold. The data of these authors on conversion to solubility, expressed in moles per liter, are given in Table 1.

The last line gives the solubility values according to the data [4].

We studied the solubility of calcium, strontium, barium, cadmium, copper and lead oxalates in aqueous solutions of potassium nitrate. The oxalate was weighed out into a flask in a quantity corresponding to 0.5 mg-equiv.; a

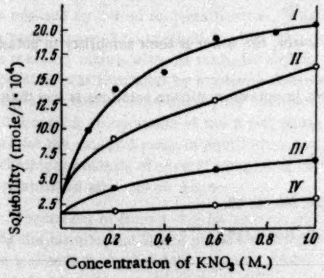

Figure 1. Dependence of solubility of oxalates of barium (I), strontium (II), cadmium (III) and copper (IV) on concentration of potassium nitrate in solution.

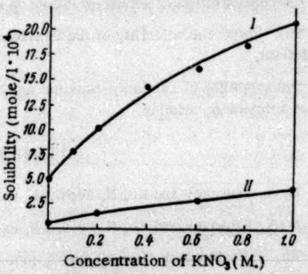

Figure 2. Dependence of solubility of oxalates of calcium (I) and lead (II) on concentration of potassium nitrate in solution.

different quantity of potassium nitrate, and then 75 ml water were added. The mixture was set aside for 7 days and was stirred periodically, several times a day; after this period had elapsed, the insoluble oxalate precipitate was filtered off, washed with 25 ml water, dissolved in sulfuric acid and titrated with a solution of potassium permanganate. Simultaneously, the volume of potassium permanganate necessary to oxidize the dried, weighed sample of the respective oxalate (control sample) was determined.

From the difference between the volume of $KMnO_4$ solution spent on the control sample and the volume of $KMnO_4$ solution spent in the oxidation of the oxalate remaining undissolved after treatment with aqueous solution, we calculated the quantity of oxalate that went into solution, in moles per liter. The experimental data are given in Table 2.

TABLE 2

Solubility of Barium, Strontium, Cadmium, Copper, Calcium and Lead Oxalates in Aqueous Solutions of Potassium Nitrate.

Concentration of KNO_3 M.	Solubility(in mole/1)					
	Ba_2CO_4	SrC_2O_4	CdC_2O_4	CuC_2O_4	CaC_2O_4	PbC_2O_4
0.0	$2.7 \cdot 10^{-4}$	$2.9 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$	$0.49 \cdot 10^{-5}$
0.1	$9.9 \cdot 10^{-4}$	—	—	—	$8.1 \cdot 10^{-5}$	—
0.2	$14.3 \cdot 10^{-4}$	$8.9 \cdot 10^{-4}$	$3.9 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$12.0 \cdot 10^{-5}$	$1.7 \cdot 10^{-5}$
0.4	$15.4 \cdot 10^{-4}$	—	—	—	$14.5 \cdot 10^{-5}$	—
0.6	$19.3 \cdot 10^{-4}$	$12.8 \cdot 10^{-4}$	$5.7 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$16.0 \cdot 10^{-5}$	$2.9 \cdot 10^{-5}$
0.8	—	—	—	—	$18.5 \cdot 10^{-5}$	—
1.0	$20.4 \cdot 10^{-4}$	$16.0 \cdot 10^{-4}$	$6.7 \cdot 10^{-4}$	$2.7 \cdot 10^{-4}$	$20.9 \cdot 10^{-5}$	$4.1 \cdot 10^{-5}$
0.0	$4.0 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$5.0 \cdot 10^{-5}$	$0.56 \cdot 10^{-5}$

The change in the solubility of barium, strontium, cadmium and copper oxalates as a function of the concentration of potassium nitrate in solution is given in Fig. 1, and that of calcium and lead oxalates is given in Fig. 2.

It may be assumed that the lower the solubility of the oxalate precipitate in water, the lower its solubility in solutions of potassium nitrate. Potassium nitrate increases the solubility of barium, strontium and calcium oxalates less than does ammonium chloride.

SUMMARY

1. The solubility of calcium, strontium, barium, cadmium, copper and lead oxalates increases with increase in the concentration of potassium nitrate in solution.

2. The lower the solubility of the individual oxalates in water, the lower is their solubility in potassium nitrate solutions.

3. The solubility of calcium, strontium and barium oxalates in potassium nitrate solutions is less than in solutions of ammonium chloride.

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INVESTIGATION OF THE TERNARY SYSTEMS $NaNO_3 - NH_4NO_3 - H_2O$, $KNO_3 - NH_4NO_3 - H_2O$, and $RbNO_3 - NH_4NO_3 - H_2O$ VIA METHODS OF PHYSICOCHEMICAL ANALYSIS AT 25°

A. S. Karnaukhov

Investigations of the ternary system of the nitrates of sodium and potassium and water were carried out by E. A. Nikitina [1], who believes that in the solid phase in the temperature range 0-100° only two salts crystallize— ammonium nitrate and sodium nitrate; investigations were also carried out by E. V. Kuklin [2], who admits the possibility of the formation of three solid phases – the two initial salts and a compound, the composition of which he does not indicate.

The solubility of the ternary system of potassium and ammonium nitrates and water has been investigated by many scientists at different temperatures, and their opinions on the nature of the solid phases that form differ markedly. Some [3-6] believe that in the solid phase in the temperature range 0 - 100° solid solutions crystallize. Other investigators [7, 8] state that a compound forms in the system of potassium and ammonium nitrates and water. A. G. Bergman and N. Butkevich [7], on investigating the solubility polytherm of the ternary system of nitrates of potassium, ammonium and water by the visual-polythermal method, indicate the formation of a compound which occupied an independent field on the diagram, which field increased with rise in temperature. S. Mukimov [8] believes that the system of potassium and ammonium nitrates and water forms a series of chemical compounds; however, none of the investigators indicate the composition of the compounds, and none give the characteristics of the solid phases. Noting the contradictory literature data, we decided to subject these systems to detailed investigation via various methods of physicochemical analysis. We also investigated the ternary system of rubidium and ammonium nitrates and water, which we are the first to study.

EXPERIMENTAL

Procedure. The investigation of the given system was carried out by an isothermal method at 25°. In order to obtain reliable solubility data, chemically pure potassium, sodium, rubidium and ammonium salts were purified by 2-fold recrystallization. Analysis of the prepared preparations showed that the purity of the salts varied from 99.54 to 99.85 %. The prepared salts were subjected to careful grinding and were placed in glass reaction vessels with oil seals, located in a water thermostat with an electric heater. The assigned temperature was regulated by a toluene thermoregulator and was maintained within ± 0.1°. With constant mixing at a constant temperature the solutions in the vessels were allowed to come to stable equilibrium, i.e. to constant composition of the liquid phase in equilibrium with the distinct solid phase. The time required for the establishment of equilibrium was determined analytically until coincidence of the results of the chemical analysis of several samples of the liquid phase. Equilibrium at 25° in the systems we investigated was established after 30-35 hours.

Specimens of from 1-2 g for analysis of the solid and liquid phases were taken simultaneously. Upon taking the sample, the liquid phase was rapidly sucked off into a pipet by a water-jet pump, and the solid phase was held in the head by a pressed filter. The head was removed, the liquid and solid phases were separately placed in small beakers with ground stoppers, cooled to room temperature, and weighed on an analytical balance. The weighed samples that were taken off in this manner were dissolved in 100 ml volumetric flasks, from which samples were taken for analytic determinations of the separate components.

Potassium was determined gravimetrically by the cobaltinitrite method in the form of $K_2NaCo(NO_2)_6$. Ammonium was determined by distillation of ammonia from alkaline solution into a known quantity of 0.1 N sulfuric acid solution, the excess of the latter being titrated with 0.1 N alkaline solution. Sodium was determined gravimetrically as the triple salt sodium zincuranylacetate; rubidium was determined gravimetrically as rubidium perchlorate from saturated solution; NO_3^- was determined by difference.

We studied the microstructure by means of a biological microscope at a magnification of 150 X. A drop of solution from the reaction vessel was placed on a slide and the crystallization was observed. The crystals that were of special interest were photographed.

Before considering the experimental material on the study of ternary systems, we deem it necessary to give a brief characterization of the solubility of the investigated salts at 25°. The solubility of ammonium nitrate, according to the data of our investigations, was 67.08%, that of sodium nitrate 47.31%, potassium nitrate 27.64% and rubidium nitrate 40.0%. The solubilities were determined on parallel samples 3-4 times, and the variations did not exceed 0.05%.

Ternary system $NaNO_3-NH_4NO_3-H_2O$. We give the data of our investigations in Table 1 and Fig. 1. The solubility isotherm of the ternary system of sodium and ammonium nitrates and water at 25° is characterized by the presence of three branches of crystallization. The first branch, from Point 1 to 6, corresponds to the formation in the solid phase of the initial sodium nitrate. The rays plotted according to the chemical composition of the solution and solid residue for Points 1-6 go toward the pole of anhydrous sodium nitrate. Point 7 is transitional, and has the composition of solution: $NaNO_3$ 28.41%, NH_4NO_3 45.52% and H_2O 26.07%.

TABLE 1

Solubility Isotherm of $NaNO_3-NH_4NO_3-H_2O$ at 25°

Liquid phase								Solid phase					
weight %				mole %		total moles H_2O/100 m. total salts	Solid residue (wt. %)				Composition of true solid phase (wt. %)	
$NaNO_3$	NH_4NO_3	total salts	H_2O	$NaNO_3$	NH_4NO_3		$NaNO_3$	NH_4NO_3	total salts	H_2O	$NaNO_3$	NH_4NO_3
47.29	—	47.29	52.71	—	—	505.2	87.91	—	87.91	12.09	100	—
42.49	11.47	53.96	46.04	77.73	22.27	397.6	85.58	2.87	88.45	11.55	100	—
35.77	22.83	58.60	41.40	59.60	40.40	325.7	73.95	9.20	83.15	16.85	100	—
32.87	30.13	63.00	37.00	50.65	49.35	268.6	76.06	9.04	85.10	14.90	100	—
29.65	36.45	66.10	33.90	43.37	56.63	234.0	69.40	14.40	83.80	16.2	100	—
25.72	42.98	68.70	31.30	36.02	63.98	207.0	72.83	16.60	89.43	10.57	100	—
28.41	45.52	73.93	26.07	37.00	63.00	160.30	40.34	40.73	81.07	18.93	67.50	32.50
25.14	47.05	72.19	27.81	33.46	66.54	174.8	50.93	37.56	88.49	11.51	67.50	32.50
23.76	46.98	70.74	29.26	32.28	67.72	187.2	51.50	37.92	89.42	10.58	67.50	32.50
22.05	47.39	69.44	30.56	30.55	69.45	199.4	44.02	42.59	86.61	13.39	63.30	36.70
21.02	48.23	69.25	30.75	29.10	70.90	209.4	44.23	40.16	84.39	15.61	67.50	32.50
21.31	51.20	72.51	27.49	28.65	71.35	170.2	7.02	83.70	90.70	9.28	—	100
11.29	60.07	71.36	28.64	15.02	84.98	—	3.40	88.00	91.40	8.60	—	100
13.00	56.00	69.00	31.00	17.93	82.07	201.6	4.51	87.37	91.88	8.12	—	100
	67.08	67.08	32.92	—	—	224.1	—	86.72	86.72	13.28	—	100

The second branch, from Point 7 to 11, corresponds to the formation of a new chemical compound. The rays that connect the chemical composition of the solution and the solid phase indicate that the composition of the double compound is $2NaNO_3 \cdot NH_4NO_3$. This compound was first established and isolated by us, and its existence was demonstrated, aside from chemical analysis, by the method of rectilinear rays of the physicochemical diagram. The composition of the solution, corresponding to eutonic Point 11, is: $NaNO_3$ 21.02%, NH_4NO_3 48.21%, H_2O 30.75%.

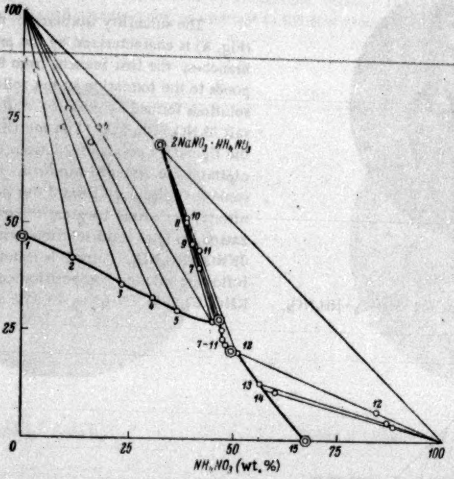

Figure 1. Solubility isotherm of system $NaNO_3-NH_4NO_3-H_2O$ at 25°. Explanation in text.

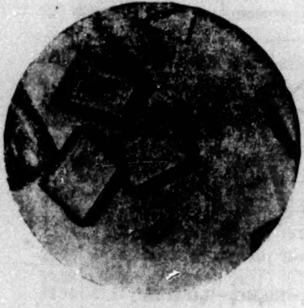

Figure 2. $NaNO_3$ crystals.

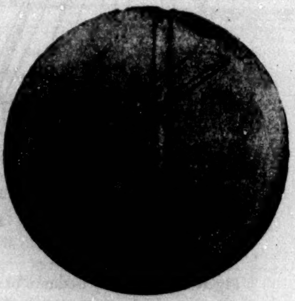

Figure 3. NH_4NO_3 crystals.

The third branch, from Point 11 to 15, corresponds to the formation of a chemically pure β-rhombic modification of ammonium nitrate. The rectilinear rays for Points 11-15 plotted according to the chemical data of the solutions and precipitates, go toward the pole of anhydrous ammonium nitrate. The double compound $2NaNO_3 \cdot NH_4NO_3$ may, by its crystalline form, be related to tetragonal syngony with corners beveled on the diagonal. Microphotographs of the crystals of the initial salts and the freshly prepared compound are given in Figs. 2-4.

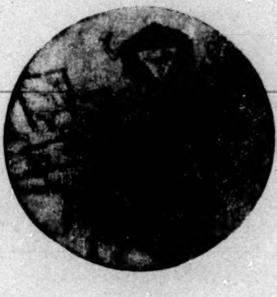

Figure 4. Crystals of the compound $2NaNO_3 \cdot NH_4NO_3$.

Ternary system $KNO_3-NH_4NO_3-H_2O$. The results of the solubility determination are given in Table 2 and Fig. 5.

The solubility isotherm of the ternary system (Fig. 5) is characterized by the presence of three branches: the first branch, from Point 1 to 8, corresponds to the formation in the solid phase of solid solutions formed by potassium nitrate and the double salt $3KNO_3 \cdot NH_4NO_3$. The rectilinear rays that connect the figurative points of solutions 2 to 8 and dry precipitates are arranged almost in parallel, though somewhat displaced toward the field of potassium nitrate, indicating its great tendency, during crystallization, to form solid solutions with a double compound $3KNO_3 \cdot NH_4NO_3$. Point 9 is transitional, and the following solution composition corresponds to it: KNO_3 22.73%, NH_4NO_3 43.81% and H_2O 34.09%.

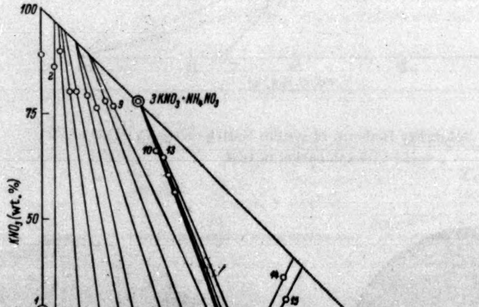

Figure 5. Solubility isotherm of the system $KNO_3-NH_4NO_3-H_2O$ at 25°. Explanation in text.

The second branch, from Point 9 to 13, corresponds to the formation of a new chemical compound. The rays that connect the chemical composition of the solution and the dry precipitates, from Point 9 to 13, converge on the line of the true solid phase at the point corresponding in composition to the double salt $3KNO_3 \cdot NH_4NO_3$. We are the first to have established and isolated this compound. Point 13 is eutonic. The composition of its solution is: KNO_3 20.00%, NH_4NO_3 47.00% and H_2O 33.00%.

The third branch from Point 13-19, corresponds to the formation of solid solutions formed by the double salt $3KNO_3 \cdot NH_4NO_3$, isomorphously absorbed by ammonium nitrate. The rays that characterize these solid solutions have a fan-shaped arrangement, in contrast to the first group of solid solutions, where they are almost

Figure 6. KNO_3 crystals.

Figure 7. Crystals of compound $3KNO_3 \cdot NH_4NO_3$.

TABLE 2

Solubility Isotherm of $KNO_3-NH_4NO_3-H_2O$ at 25°.

Liquid phase							Solid phase					
% by weight				mole %		Moles H_2O/100 moles total salts	% by weight				Composition of true solid phase (wt. %)	
KNO_3	NH_4NO_3	total salts	H_2O	KNO_3	NH_4NO_3		KNO_3	NH_4NO_3	total salts	H_2O	KNO_3	NH_4NO_3
27.64	—	27.64	72.36	100.00	—	1472.40	89.13	—	89.13	10.87	—	—
25.67	3.30	28.97	71.03	86.10	13.90	1340.00	85.82	2.68	88.50	11.50	98.00	2.00
25.50	9.00	34.50	65.50	70.00	30.00	1000.00	90.04	3.40	93.44	6.56	97.00	3.00
25.20	13.61	38.81	61.19	59.42	40.58	811.45	79.83	5.86	85.69	14.31	96.50	3.50
25.05	18.64	43.69	56.31	51.56	48.44	650.70	80.03	7.50	87.53	12.47	95.50	4.50
24.05	22.25	46.30	53.70	46.02	53.98	580.00	79.00	10.23	83.23	10.77	93.50	6.50
23.22	29.01	52.23	47.77	38.85	61.15	447.60	76.00	12.61	88.61	11.39	92.50	7.50
22.00	35.00	57.00	43.00	33.20	66.80	367.00	83.00	12.00	95.00	5.00	91.00	9.00
22.73	43.18	65.91	34.09	29.41	70.59	248.30	66.11	26.25	92.36	7.64	78.75	21.25
21.27	44.10	65.37	34.63	27.60	72.40	249.60	56.00	30.50	86.50	13.50	78.75	21.25
19.28	46.21	65.49	34.51	24.77	75.23	250.00	60.03	29.30	84.33	10.67	78.75	21.25
19.94	47.31	67.25	32.75	25.00	75.00	231.00	64.36	27.86	92.22	7.78	78.75	21.25
20.00	47.00	67.00	33.00	25.22	74.78	233.10	56.86	32.42	89.28	10.72	78.75	21.25
18.83	48.53	67.36	32.64	23.37	76.63	227.40	36.10	57.25	93.35	6.65	40.50	59.50
17.04	49.80	66.84	32.16	21.26	78.74	227.80	31.16	57.44	88.60	11.40	36.00	64.00
15.31	52.33	67.64	32.36	18.75	81.25	223.60	22.59	69.23	91.82	8.18	25.00	75.00
12.14	56.80	68.94	31.06	15.00	85.00	206.00	14.32	76.60	90.92	9.08	15.00	85.00
6.61	61.80	68.41	31.59	7.76	92.24	209.00	7.50	84.36	91.86	8.14	8.00	92.00
—	67.08	67.08	32.92	—	100.00	218.00	—	—	—	—	—	—

parallel. The quantity of ammonium nitrate in this group of solid solutions varies in the range 49.53-62.00%. The solubility branch along which the first group of solid solutions forms is considerably larger than the branch of solid solutions formed by ammonium nitrate and the double compound $3KNO_3 \cdot NH_4NO_3$. Thus, the solubility isotherm which we obtained for the ternary system of potassium and ammonium nitrates and water indicates that at 25° the system $KNO_3-NH_4NO_3-H_2O$ forms a double compound with bilateral solid solutions.

The microstructures of initial salts and the newly prepared compound $3KNO_3 \cdot NH_4NO_3$ were investigated. Data on the study of the microstructure are given in Figs. 4, 6 and 7. Potassium nitrate most often crystallized in the form of orthorhombic syngony. Ammonium nitrate upon crystallization from solution at a temperature of from 0 to 40°, separates out in the form of the β-rhombic modification. The newly prepared compound $3KNO_3 \cdot NH_4NO_3$ (Fig. 7) sharply differs from the initial salts in its crystalline form. These crystals have the form of rectilinear tetrahedrons.

Ternary system $RbNO_3-NH_4NO_3-H_2O$ was first studied by us. The data of the investigations are given in Table 3 and Fig. 8.

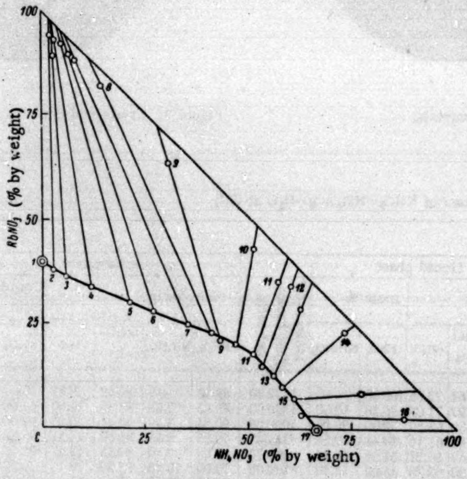

Figure 8. Solubility isotherms of the system $RbNO_3-NH_4NO_3-H_2O$ at 25°. Explanation in text.

The ternary system of rubidium and ammonium nitrates and water is characterized by the presence of a continuous series of solid solutions; therefore, the interconnected figurative points of the solution gave a regular curve consisting of one branch.

The arrangement of rays on the diagram indicates that two groups of solid solutions form in the system. The first group of solid solutions borders on the region of rubidium nitrate; the rectilinear rays of equilibrium solutions and dry precipitates are considerably displaced to the side of the rubidium nitrate pole. This indicates that the solid phase is richer in rubidium nitrate than is the solution in equilibrium with it. The direction of the rectilinear rays makes it possible to conclude that at these concentrations rubidium nitrate displays a strong tendency toward the formation of solid solutions, isomorphously absorbed by ammonium nitrate. The portion of

TABLE 3

Solubility Isotherm of the System $RbNO_3-NH_4NO_3-H_2O$ at 25°.

Liquid phase							Solid phase					
% by weight				Mole %		Moles H_2O/100 moles total salts	% by weight				Composition of true solid phase (wt. %)	
$RbNO_3$	NH_4NO_3	total salts	H_2O	$RbNO_3$	NH_4NO_3		$RbNO_3$	NH_4NO_3	total salts	H_2O	$RbNO_3$	NH_4NO_3
40.00	—	40.00	60.00	100.00	—	1233.30	—	—	—	—	100.00	—
38.36	3.00	41.36	58.64	87.54	12.46	1100.00	94.2	1.80	96.00	4.00	98.50	1.50
36.55	5.82	42.37	57.63	77.00	23.00	1025.60	93.20	2.41	95.61	4.39	98.00	2.00
34.42	12.59	47.01	52.99	80.14	19.96	1024.40	92.74	2.80	95.54	4.46	97.50	2.50
29.82	21.06	50.88	49.12	42.20	56.80	950.00	91.74	5.0	96.74	3.26	95.50	4.50
28.46	26.66	55.12	44.88	36.60	63.40	476.20	89.86	6.84	96.50	3.50	94.50	5.50
24.97	34.93	59.90	40.10	28.05	71.95	368.00	88.56	8.38	96.94	3.06	92.50	7.50
22.81	41.56	54.37	35.63	22.40	77.60	300.00	82.60	14.00	96.60	3.40	89.00	11.00
21.44	43.51	64.95	35.05	21.04	78.96	300.00	64.20	30.00	94.20	5.80	73.50	26.50
19.48	47.31	66.79	33.21	18.26	81.74	254.50	42.77	51.23	94.00	6.00	49.0	51.0
17.65	50.62	68.27	31.73	15.94	84.06	233.80	35.07	56.90	91.97	8.03	41.00	59.00
15.23	52.70	67.93	32.07	13.50	86.50	236.00	34.20	60.47	94.67	5.33	38.50	61.50
13.39	55.70	69.09	30.91	11.56	88.44	218.50	28.56	62.61	91.17	8.83	35.00	65.00
10.03	58.42	68.45	31.55	8.75	91.25	220.00	23.15	73.34	96.49	3.51	24.50	75.50
6.97	61.55	68.52	31.48	5.75	94.25	213.00	7.81	77.12	84.93	15.07	8.50	91.50
3.51	63.69	67.20	32.80	2.88	97.12	222.00	2.55	87.93	90.48	9.52	2.00	98.00
—	67.08	67.08	32.92	—	100	—	—	—	—	—	—	—

the curve from Point 10 to 17 indicates the formation of the second group of solid solutions formed by ammonium nitrate, with isomorphously included rubidium nitrate. The rectilinear rays that characterize this group of solid solutions have a fanlike arrangement in contrast to the first group of solid solutions of this system. The solubility branch corresponding to the formation of the first group of solid solutions is somewhat larger than the solubility branch of the solid solutions formed by ammonium nitrate with isomorphously included rubidium nitrate. The formation of continuous solid solutions in the ternary system of rubidium and ammonium nitrates and water is due to the closeness in the dimensions of the ionic radii of the elements that enter into this system, and also to the analogous crystal structures of rubidium and ammonium nitrates (ionic radii: Rb^+ 1.49, NH_4^+ 1.43 A). Rubidium and ammonium nitrates crystallize in rhombic syngony from saturated solutions at 25°.

SUMMARY

1. Three ternary systems have been studied at 25°: $NaNO_3-NH_4NO_3-H_2O$, $KNO_3-NH_4NO_3-H_2O$ and $RbNO_3-NH_4NO_3-H_2O$.

2. The obtained double compound $2NaNO_3 \cdot NH_4NO_3$ sharply differs in crystalline form from the initial salts and is characterized by tetragonal syngony with beveled angles along the diagonal.

3. The ternary system $KNO_3-NH_4NO_3-H_2O$ in aqueous solutions at 25° forms a double compound and bilateral solid solutions, formed from one side by potassium nitrate with the double compound $3KNO_3 \cdot NH_4NO_3$, and from the other side by ammonium nitrate and a double salt.

The double compound $3KNO_3 \cdot NH_4NO_3$ sharply differs in crystalline form from the initial salt;

4. The formation of continuous solid solutions in the ternary system $RbNO_3-NH_4NO_3-H_2O$ at 25° is due to the closeness in the dimensions of the ionic radii of the elements that enter into this system, and also to the analogous crystal structures of rubidium and ammonium nitrates.

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DETERMINATION OF THE ISOTOPIC OXYGEN COMPOSITION IN ORGANIC COMPOUNDS

R. V. Kudryavtsev, B. V. Ottesen and D. N. Kursanov

The problem of determining the proportion of oxygen isotopes in organic compounds is subdivided into two major operations: 1) the isolation of oxygen from the organic substance in a form convenient for isotopic analysis, and 2) the isotopic analysis of the oxygen in the obtained compound. *

Up to now the problem of isolating oxygen from organic substances in a form convenient for isotopic analysis has been solved differently by different authors – depending on the character of the studied substance.

With such a situation an investigator, using the heavy oxygen isotope in his work, is exposed to great difficulties, associated with the need of selecting and becoming familiar with the various methods, depending on the character of the substances under investigation.

The direct isotopic analysis of oxygen in substances, isolated by various methods from organic compounds, has been developed to a much greater degree. Such substances are usually either water or carbon dioxide.

If the analyzed water fails to contain an excess of the heavy hydrogen isotope, then the ratio of the oxygen isotopes can be determined densimetrically. The use of the densimetric method for the analysis of oxygen isotopes in water is complicated by the need for the most thorough removal of organic impurities from the water. Such a purification is unavoidably associated with the use of oxidizing agents, the oxygen of which, exchanging with the oxygen of the investigated water, introduces considerable error into the analysis results. According to the data of Cohn and Urey [1], the errors ensuing when the isotopic composition of the oxygen in water is analyzed by this method can reach 15-20%.

The isotopic analysis of the oxygen in carbon dioxide is a more reliable and rapid method. Here it is run by the mass spectrometric method, and, despite the fairly complicated apparatus, is so convenient that this method is used not only in those cases where carbon dioxide is isolated directly from the organic compound,** but also in those cases where water is isolated from the organic compound.*** For this purpose a known amount of carbon dioxide, containing the natural proportion of oxygen isotopes (O^{16} = 99.76%, O^{18} = 0.2%, O^{17} = 0.04%), is added to a definite amount of the investigated water. Shaking of the water vapors and carbon dioxide results in achieving equilibrium for the isotopic composition of the oxygen in the water and carbon dioxide [1]:

$$H_2O^{18} + CO_2^{16} \rightleftharpoons H_2O^{16} + CO^{16}O^{18}.$$

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* Here, as later, the direct determination of the proportion of oxygen isotopes in the organic substance is discussed, and not their difference, as is frequently done when the oxygen exchange of organic compounds is studied, where the amount of O^{18} in the organic substance is judged by the decrease in the amount of O^{18} in the taken water.

** For example, by decarboxylation.

*** For example, by hydrogenation.

The isotopic composition of the carbon dioxide, obtained after equilibrition, is analyzed by the mass spectrometric method. Knowing the amounts of water and carbon dioxide, taken for equilibration, and also the isotopic composition of the carbon dioxide before and after equilibration and the coefficient for the distribution of O^{18} between water and carbon dioxide, it is a simple matter to calculate the initial isotopic composition of the oxygen in the water.

The purpose of the present communication is to describe the method developed by us for the isolation of oxygen from organic compounds in a form convenient for isotopic analysis.

In order for such a method to find successful application, it should satisfy the following prerequisites.

1. The error in determining the isotopic oxygen composition, arising in the isolation of oxygen (in the form of either water or CO_2) from organic compounds, should be minimal.

2. The method should be as highly universal as possible.

3. In isolating oxygen from organic compounds it is desirable that the obtained substance (either water or CO_2) fail to come in contact with substances that contain oxygen capable of exchange. In the opposite case, if the exchange is not discounted, the whole analysis result can stand in doubt.

To isolate oxygen from organic compounds we decided to use the method of exhaustive destructive hydrogenation over nickel catalyst in a stream of hydrogen. The selection of metallic nickel as catalyst was conditioned by the need to use oxygen-free agents so as to prevent the possibility of oxygen exchange between the obtained water and the catalyst.

The nickel catalyst, prepared by the alkali leaching of a 50% nickel-50% aluminum alloy, proved to be completely suitable for the exhaustive hydrogenation of oxygen-containing organic compounds. In addition, this catalyst possesses the extremely valuable trait of showing good reproducibility of properties when prepared under standard conditions.

The alkali leaching of the catalyst and the removal of the alkali and aluminum oxide from it by washing were done with extreme care; however, all of the attempts made to obtain a catalyst completely devoid of oxygen proved unsuccessful.

TABLE 1

Exchange Capacity of the Oxygen in Molybdenum Glass at 300° (Number of passes – 2)

Amount of O^{18} in the water (in %)	
Before passage	After passage
1.30	1.26
0.20	0.20
1.30	1.28
0.20	0.20

Being assured that the hydrogen, used for hydrogenation, was devoid of both water and oxygen, we studied the exchange capacity of the oxygen in the walls of the catalyst tube with heavy oxygen water at 300 and 400°. Heavy oxygen water with a known content of the heavy oxygen isotope and ordinary water were alternately passed in a hydrogen stream through a heated empty glass tube. If the oxygen of the glass showed exchange with the oxygen of the taken water, then the concentration of the heavy oxygen isotope in the heavy water should show a decrease, and the concentration of O^{18} in the light water should show an increase. It was revealed that the oxygen present in the walls of the tube made from molybdenum glass * failed to show exchange with the oxygen in water at either 300° or at 400° (Table 1).

After this about 60 g of catalyst was charged into the tube, and it was then subjected to a similar study. The results of these experiments, shown in Table 2, indicate the presence of exchange-capacity properties for the oxygen found in the catalyst, which first shows exchange by the heavy isotope, reducing the O^{18} concentration in the water, and then, when ordinary water is passed, shows exchange by the lighter isotope, making the water heavier.**

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* Composition of the glass in %: SiO_2 68, B_2O_3 20, Al_2O_3 3, Na_2O 4, K_2O 5.

** The possibility of incomplete drying of the catalyst and ends of the tube was excluded by extending the drying time and making sure that the ends of the tube had been properly heated.

Since the attempt to prepare an oxygen-free nickel catalyst from the Ni-Al alloy ended in failure, while the catalyst, obtained by the reduction of nickel oxide, proved to be insufficiently active, we decided to limit ourselves to reducing the amount of oxygen in the catalyst to a minimum. To achieve this we subjected the catalyst to further vigorous leaching with alkali and also reduced considerably the amount of catalyst charged into the tube for hydrogenation.

TABLE 2

Exchange Capacity of the Oxygen in the Catalyst (Amount of catalyst – 60 g; number of passes – 1)

Amount of water	Amount of O^{18} in the water (in %)	
	Before passage	After passage
0.5	1.50	0.43°
0.5	1.50	0.89
0.4	0.20	0.78
0.5	1.50	0.24
0.5	0.20	1.12
0.35	1.50	0.23
0.5	1.50	0.57
0.6	0.20	0.44
0.5	1.50	0.29
0.4	1.50	0.56

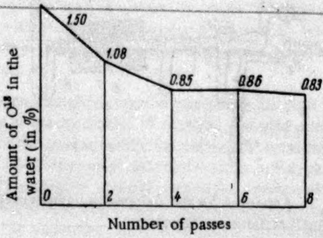

Figure 1. Change in the concentration of O^{18} in heavy-oxygen water when passed over the catalyst.

Determination of the minimum amount of catalyst, sufficient to achieve fairly rapid hydrogenation and also assure complete conversion of the substance into water after a single pass over the catalyst, revealed that about 1 g is sufficient for this purpose.

Further leaching of the catalyst consisted in the following: 20-25 g of the catalyst, prepared by the method described above, was placed in a 200 ml porcelain beaker and covered with 70 ml of 40% NaOH, after which the mixture was vigorously stirred for 30-40 minutes under heating at the boil, and then washed 2-3 times with water. This sequence of operations was repeated 9 times. After leaching, the catalyst was repeatedly washed, first with tap water, and then with distilled water.

The next step in the development of a method for the isolation of oxygen from organic compounds for isotopic analysis was the exact determination of the amount of exchange-capacity oxygen in the given catalyst portion and the quantitative calculation of the amount of dilution of the oxygen in the investigated water by the oxygen of the catalyst. We used the isotopic method to determine the amount of exchange-capacity oxygen in the catalyst, equilibrating the isotopic composition of the oxygen in the catalyst and in the water, H_2O^{18}, passed through the catalyst especially for this purpose. It was revealed that to achieve equilibrium in the isotopic exchange reaction between 0.5 g of water and the aluminum oxide found in ~ 1 g of nickel catalyst, it is sufficient to pass this water 4 times over the catalyst in vacuo. When heavy oxygen water is passed over the catalyst at 300° the O^{18} concentration in the water varies as a function of the number of passes, as is shown in Fig. 1.

The amount of exchange-capacity oxygen present in the catalyst (K) can be calculated with the aid of the equation:

$$K = \frac{a\,(Y - X)}{X - 0.2}, \qquad (1)$$

where a is the amount of oxygen in the passed water (in g), Y is the O^{18} concentration in the water prior to passage (in our experiments Y = 1.50 atom %), X is the O^{18} concentration in the water after passage (in atom %) and 0.2 is the O^{18} concentration in the oxygen of the catalyst prior to experiment (natural).

Knowing the amount of exchange-capacity oxygen in a given catalyst portion and the time needed to attain equilibrium in the isotopic exchange reaction between water and aluminum oxide, it becomes possible to quantitatively solve the problem of the influence shown by the isotopic exchange (between the oxygen of the catalyst and the oxygen of the obtained water) on the O^{18} concentration in this water.

If the O^{18} concentration in the water prior to its passage over the catalyst is unknown, then from Equation (1) we obtain:

$$Y = \frac{X(K+a) - K \cdot 0.2}{a}. \quad (2)$$

For the exhaustive hydrogenation of organic compounds and to equilibrate the isotopic composition of the obtained water with the oxygen of the catalyst we constructed the apparatus shown in Fig. 2.

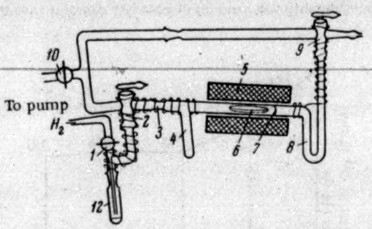

Figure 2. Apparatus for the exhaustive hydrogenation of an analyzed organic substance. Explanation in the text.

The investigated substance is placed in the test tube with sidearm 12. The air is removed, and the substance in a stream of pure dry hydrogen is passed through furnace 5, heated to 300°. The hydrogenation products are trapped in the U-shaped tube 8, cooled with liquid nitrogen, while the excess hydrogen is removed through stopcock 9, fitted with the usual gooseneck.

On conclusion of hydrogenation the stopcocks 1 and 2 are closed, and the cooled U-shaped tube 8 is taken out. Heating of this tube to room temperature results in the removal of the organic portion of the hydrogenation products (methane, ethane, propane). After this, stopcock 9 is closed, the U-shaped tube is again cooled with liquid nitrogen and the system from stopcock 2 to stopcock 9 is evacuated to a pressure of $2-7 \cdot 10^{-3}$ mm; the evacuation is through stopcock 9. The porous partition 7, sealed in the tube, is necessary for the reason that in case of insufficiently smooth opening of stopcock 9, the catalyst, found in boat 6, is not sprayed into the U-shaped tube. Then stopcock 9 is closed, the heating of finger 4 is discontinued, and also the cooling of the U-shaped tube 8. Finger 4 is cooled with liquid nitrogen, while the U-shaped tube is warmed slightly. The water is distilled into finger 4, and then again into the U-shaped tube. In the meantime the space between stopcocks 1 and 2 is also evacuated to a pressure of $2-7 \cdot 10^{-3}$ mm, and the water is distilled for the last time from the U-shaped tube into the test tube 12, which is removed from the apparatus.

Both during the hydrogenation period and in the subsequent equilibration it is important to avoid condensation of the vapors of the passed liquid in the stopcocks, on the sidearm and on the walls of the tube. For this, stopcocks 1, 2 and 9, sidearm 3, and also the portion of the tube emerging from the furnace were wrapped with nichrome wire and heated to 170-180°.

The vast majority of the vacuum greases, used in contemporary laboratory practice, are not heat stable when heated: they change their consistency and copiously evolve gases. We used a heat-stable silicone vacuum grease for lubricating the stopcocks.

It is necessary to normalize the isotopic composition of the oxygen found in the catalyst after each experiment, i.e. to bring the proportion of the oxygen isotopes found in the catalyst to the natural ratio. In the opposite case it proves impossible to use the above equations for the calculations. To normalize the composition of the oxygen isotopes in the catalyst it is sufficient to pass through the system, while in a working condition (usually immediately after the experiment), a known amount of distilled water vapors, containing the natural proportion of oxygen isotopes. If the catalyst contains ~0.1 g of exchange-capacity oxygen,* then, as both calculation and experiment show, 0.6 g of distilled water is sufficient to completely "wash out" the excess heavy oxygen isotope from the catalyst. In all of our experiments we "washed" the catalyst with the vapors of 1.5-2.0 g of distilled water – an amount more than sufficient to normalize the composition of the oxygen isotopes in the catalyst.

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* Actually it was usually only ½ of this.

The total error of the whole analysis for the composition of the oxygen isotopes found in organic compounds fails to exceed ±3-4% of the measured value. Into this enter: 1) the possibly imperfect hydrogen purification (here the error is not greater than 1%), 2) the inaccuracy of determining the amount of exchange-capacity oxygen present in the catalyst (error ~1%), and 3) the error of the mass spectrometric analysis – of the order of 1%.

Making use of the developed method, we found it possible to analyze a series of oxygen-containing substances – representing various classes of organic compounds – for their isotopic oxygen composition. We analyzed the following compounds for their isotopic composition: methyl, ethyl, isopropyl, n-butyl and n-hexyl alcohols, propionic acid, ethyl propionate, dimethyl ether and acetaldehyde.

As a result, our method permits analyzing various oxygen-containing organic compounds for their isotopic oxygen composition; here we were able to escape from most of the theoretical limitations, assumed prior to us by many investigators. However, the application limits of the present method should also be mentioned. First, the use of a nickel catalyst excludes the possibility of analyzing compounds that contain sulfur, phosphorus, halogens, etc., since this would lead to poisoning of the catalyst. Second, due to the absence of suitable greases for the stopcocks it is difficult to analyze substances that show a rather high boiling point (above 200°), since this would lead to retention of the substance in the stopcocks. Third, and finally, difficulties associated with the individual characteristics of the analyzed substance and its behavior toward hydrogenation under the given conditions should be encountered, and already have been encountered. For example, several attempts made to hydrogenate benzyl alcohol and acetone proved unsuccessful. The reason for this is still obscure.

SUMMARY

A method has been described for determining the isotopic oxygen composition of organic compounds via the method of exhaustive hydrogenation over a skeletal nickel catalyst and subsequent mass spectrometric analysis.

LITERATURE CITED

[1] M. Cohn and H. C. Urey, J. Am. Chem. Soc. 60, 679(1938).

The total error of the whole analysis for all compounds. [illegible] oxygen isotope [illegible] compounds fails to exceed ±5% of the [illegible] value. [illegible] the [illegible] exceed [illegible]; 2) the [illegible] of determining the amount of [illegible] in the [illegible], and 3) the error of the mass-spectrometric analysis of the order of 1%.

Making use of the above procedure, we made an attempt to analyze a series of oxygen-containing substances representing various classes of organic compounds with [illegible] isotope composition. We analyzed the following compounds for their isotopic composition: [illegible], propionic acid, ethyl propionate, [illegible] ether and [illegible].

As a result, our control [illegible] analyzing various oxygen-containing organic compounds for their isotopic oxygen composition, we were able to escape from most of the theoretical limitations assumed prior to in [illegible] investigations. However, the approximate results of the present method must also be emphasized. First, the use of a nickel catalyst excludes the possibility of analyzing oxygen-containing compounds, [illegible], halogens, etc., which [illegible] lead to poisoning of the catalyst. Second, due to the absence of [illegible] able grounds for the [illegible] analysis [illegible] that show a rather high [illegible] 200°), since this would lead to [illegible] of the compound. Third, and finally, difficulties associated with the individual characteristics of the analyzed substances [illegible] given conditions should be [illegible] have been [illegible]. For example, several attempts made to hydrogenate [illegible]. The reason for this is still obscure.

SUMMARY

A method has been described for determining the isotopic oxygen composition of organic compounds by the method of [illegible] hydrogenation over a nickel catalyst and subsequent mass-spectrometric analysis.

LITERATURE CITED

[1] [illegible] J. Am. Chem. Soc. [illegible]

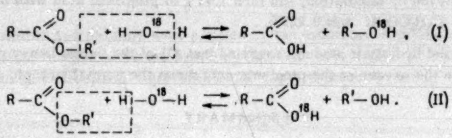
STUDY OF THE MECHANISM OF HYDROLYSIS WITH THE AID OF THE HEAVY OXYGEN ISOTOPE

I. HYDROLYSIS OF ETHYL PROPIONATE IN ALKALINE MEDIUM

D. N. Kursanov and R. V. Kudryavtsev

The question of the location of bond rupture in the hydrolysis of esters has been repeatedly studied. However, prior to the discovery of the heavy oxygen isotope, it was impossible to obtain a direct answer to this question. The hydrolysis reaction can proceed in accord with one of two schemes (or simultaneously by both schemes).

If the hydrolysis is run with water, the oxygen of which has been enriched in the heavy isotope, then as a reaction result the excess O^{18} proves to be either in the alcohol or in the acid, depending on where bond rupture occurred.



$$R-C\overset{O}{\underset{O-R'}{\langle}} + H-O^{18}-H \rightleftarrows R-C\overset{O}{\underset{OH}{\langle}} + R'-O^{18}H\,, \quad (I).$$

$$R-C\overset{O}{\underset{O-R'}{\langle}} + H-O^{18}-H \rightleftarrows R-C\overset{O}{\underset{O^{18}H}{\langle}} + R'-OH\,. \quad (II).$$

If the reaction proceeds simultaneously by Schemes (I) and (II), then the heavy oxygen isotope is found to be distributed between both hydrolysis products.

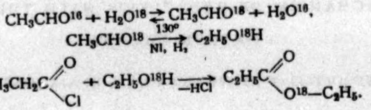
In 1934 Polanyi and Szabo[1] made an attempt to study the mechanism of the alkaline hydrolysis of amyl acetate in the presence of heavy oxygen water. Having run the hydrolysis, the authors isolated the amyl alcohol and on dehydrating it found that the water obtained here shows the normal isotopic composition. The isotopic composition of the acetic acid was not studied by the authors. It would seem that the question is clear: if the heavy oxygen isotope fails to be found in the alcohol, then it must be present in the acid; consequently, in the alkaline hydrolysis of amyl acetate the rupture is at the acyl-oxygen bonds. The above authors also came to the same conclusion, and results of their work were repeatedly mentioned later in various textbooks, monographs and papers.

However, even though the statement made by Polanyi and Szabo, as will be shown later, proved to be valid, still it fails to follow logically from the experimental data obtained by these authors. The truth of the matter is that the dehydration of the amyl alcohol was run over aluminum oxide (bauxite) heated to 400°, and even if an excess of the heavy oxygen isotope was present in the amyl alcohol, still its presence in the obtained water could have hardly been shown due to the ease with which the exchange of oxygen between the obtained water and the aluminum oxide takes place under these conditions.

This finds confirmation in the data of the experiments performed by Mills and Hindin [2], who studied the isotopic exchange reaction between heavy oxygen water and aluminum oxide and established that it takes place under the above-described conditions.

As a result, the conclusion of Polanyi and Szabo relative to rupture taking place at the acyl-oxygen bonds in the alkaline hydrolysis of amyl acetate must be regarded as being without sufficient basis, and requires further verification.

These considerations caused us to undertake an experimental study of the question as to the location of bond rupture in the alkaline hydrolysis of carboxylic acid esters. As our study subject we selected ethyl propionate, containing an excess of the heavy oxygen isotope. We synthesized this ester by the following scheme:



$$CH_3CHO^{16} + H_2O^{18} \rightleftarrows CH_3CHO^{18} + H_2O^{16},$$

$$CH_3CHO^{18} \xrightarrow[Ni,\ H_2]{130^\circ} C_2H_5O^{18}H$$

$$CH_3CH_2C\overset{O}{\underset{Cl}{}} + C_2H_5O^{18}H \xrightarrow[-HCl]{} C_2H_5C\overset{O}{\underset{O^{18}-C_2H_5.}{}}$$

We ran the hydrolysis of the ethyl propionate with ordinary water in the presence of alkali.

In a flask (having a capacity of ~20 ml) we placed 2.16 g of sodium hydroxide (c. p.), 5.05 g of water (distilled twice) and 5 g of ethyl propionate, containing 0.2% of O^{18} in the C-O group and 0.71% of O^{18} in the $O-C_2H_5$ group. After heating for several hours under reflux the ethyl alcohol was distilled off, after which it was dehydrated and redistilled. n_D^{20} 1.3620, d_4^{20} 0.7896. The amount of O^{18} (in the alcohol) was 0.71%.

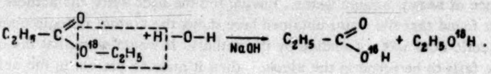
After distilling off most of the alcohol the residue in the reaction flask is composed of C_2H_5COONa, NaOH, H_2O and traces of alcohol. The water and residual alcohol were vacuum distilled nearly to dryness, after which 2.9 ml of concentrated sulfuric acid was added. The propionic acid that separated here was percolated with benzene, the benzene removed by distillation, and then 1.47 g of propionic acid with b. p. 138-139° was collected. The amount of O^{18} in the C_2H_5COOH was 0.212%.

Isotopic analysis of the hydrolysis products revealed that all of the excess heavy oxygen isotope is contained in the ethyl alcohol, while the oxygen of the propionic acid shows the normal isotopic composition.

SUMMARY

Ethyl propionate, containing an excess of heavy oxygen, was synthesized.

Isotopic analysis of the alkaline hydrolysis products of this ester revealed that the excess of the heavy oxygen isotope is found in the ethyl alcohol, and, consequently, in the hydrolysis the rupture takes place at the acyl-oxygen bonds in accord with the scheme:



$$C_2H_5-C\overset{O}{\underset{O^{18}-C_2H_5}{}} + H-O-H \xrightarrow[NaOH]{} C_2H_5-C\overset{O}{\underset{O^{16}H}{}} + C_2H_5O^{18}H.$$

LITERATURE CITED

[1] M. Polanyi and A. L. Szabo, Trans. Faraday Soc. 30, 508 (1934).

[2] G. A. Mills and S. G. Hindin, J. Am. Chem. Soc. 72, 5549 (1950).

Received May 23, 1955.

THE ELECTRICAL CONDUCTIVITY OF TERNARY SYSTEMS COMPOSED OF AMINES, ACETIC ACID AND WATER

S. P. Miskidzhyan and I. A. Volina

Systems, composed of amines, acid and water have long served as subjects to attract the attention of electrochemists from the viewpoint of their utilization for the preparation of various oxidation and reduction products of amines by electrolysis [1].

The purpose of our work was to study the electrical conductivity of a number of ternary systems, composed of amines (aniline, quinoline, pyridine), acetic acid and water, with the formation of complexes in them being taken into consideration. We failed to find any data in the literature on the electrical conductivity of the indicated ternary systems. Only for the system aniline-acetic acid-water do the data of Pound [2] exist, who, although measuring the electrical conductivity of a large number of solutions of the indicated system, failed to take into consideration interaction between the components of the system.

EXPERIMENTAL

The aniline, quinoline and pyridine were purified by the technique of drying them over potassium hydroxide and subsequent distillation. For our work the following fractions were taken: aniline 183-184°, quinoline 283°, and pyridine 115°. Their specific gravities at 20° were respectively 1.022, 1.0939 and 0.984. The acetic

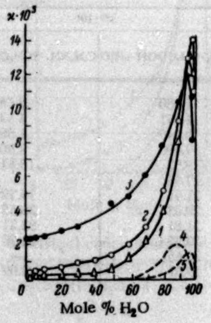


Figure 1. Electrical conductivities of the systems: 1) $C_9H_7N \cdot CH_3COOH-H_2O$; 2) $C_9H_7N \cdot 2CH_3COOH-H_2O$; 3) 12 mole % C_9H_7N and 88 mole % $CH_3COOH-H_2O$; 4) $C_9H_7N-CH_3COOH$; 5) $CH_3COOH-H_2O$.

TABLE 1

Amount of H_2O (in mole %)	Specific electrical conductivity $\kappa^{20} \cdot 10^3$	
	$C_9H_7N \cdot CH_3COOH-H_2O$	$C_9H_7N \cdot 2CH_3COOH-H_2O$
2	0.0431	0.4233
5	0.0581	0.4786
10	0.0616	0.5282
20	0.0789	0.6593
30	0.1859	1.008
40	0.3950	1.138
50	0.5986	1.518
60	1.201	2.143
70	2.256	3.148
80	3.919	5.141
90	8.016	9.397
95	13.0	13.19
98	12.02	14.32
99	—	11.405

acid was obtained from the commercial grade of glacial acetic acid by the technique of repeated freezings. The acid obtained in this manner had m. p. 16.45°. The water that we used had been distilled twice. The mixtures were prepared by the gravimetric technique, and stored in special dark-colored flasks fitted with ground-glass stoppers, which, in turn, were kept in a desiccator. The electrical conductivity of these mixtures was measured in the usual manner at 20 ± 2°.

Quinoline-Acetic Acid-Water System

Puschin and Rikovski [3] studied the binary quinoline-acetic acid system by the fusion method, and Puschin and Matavulj [4] studied it by the refractive index method. The diagrams of these properties indicate that two compounds are formed in the system: $C_9H_7N \cdot CH_3COOH$ and $C_9H_7N \cdot 2CH_3COOH$, both showing thermal decomposition into their components. Proceeding from this, we consider it expedient to study the solutions, corresponding to the composition of these compounds, in water.* In view of the fact that the specific electrical conductivity isotherm of solutions of the binary system quinoline-acetic acid, studied by Puschin and Tutundzhic [5], shows a maximum, corresponding to a composition of 12 mole % quinoline, we deemed it necessary to also measure the electrical conductivity of this solution in water.

Our measurement results for the specific electrical conductivities of all of these solutions are given in Table 1 and plotted in Fig. 1.

For the sake of comparison we have also shown by dotted lines in Fig. 1 the specific electrical conductivity isotherms for the binary systems: quinoline-acetic acid, based on the data of Puschin and Tutundzhic [5], and acetic acid-water, based on the data of N. A. Trifonov and S. I. Cherbov [6].

Aniline-Acetic Acid-Water System

The physicochemical analysis method has been used to study many of the properties of the binary system aniline-acetic acid [7-9]. The diagrams of all of the studied properties agree in indicating the formation in the system of a compound with composition $C_6H_5NH_2 \cdot 2CH_3COOH$. Only a few authors also indicate the formation of a second compound with the composition $C_6H_5NH_2 \cdot CH_3COOH$.

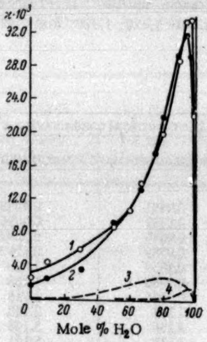


Figure 2. Electrical conductivities of the systems: 1) $C_6H_5NH_2 \cdot 2CH_3COOH-H_2O$; 2) $C_6H_5NH_2 \cdot CH_3COOH-H_2O$; 3) $CH_3COOH-C_6H_5NH_2$; 4) $CH_3COOH-H_2O$.

TABLE 2

Amount of H_2O (in mole %)	$\varkappa^{20} \cdot 10^3$	
	$C_6H_5NH_2 \cdot CH_3COOH-H_2O$	$C_6H_5NH_2 \cdot 2CH_3COOH-H_2O$
0.0	1.980	2.580
10.0	2.471	4.541
30.0	3.540	5.886
50.0	9.086	8.804
67.0	13.52	13.81
75.0	17.68	—
80.0	21.91	19.72
90.0	29.03	28.63
95.0	31.81	33.21
97.0	29.35	33.26
98.0	26.65	—
99.0	19.81	22.09

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* We discount the possibility of interaction in the acetic acid-water system, since at the present time there fail to exist reliable data, testifying to the presence of interaction between them, while our taken amines are practically immiscible with water, with the exception of pyridine, which, although it is completely miscible with water, still apparently fails to show reaction with it, or else reacts very slightly.

The maximum on the specific electrical conductivity isotherm is found at 33 mole % aniline, i.e. it corresponds to the composition of the compound

$$C_6H_5NH_2 \cdot 2CH_3COOH.$$

In connection with this we prepared solutions for our measurements, corresponding to the composition of these compounds with water, i.e. (33.3 mole % aniline + 66.7% mole % acetic acid)-water and (50 mole % aniline + 50 mole % acetic acid)-water.

The data, obtained by us in measuring the specific electrical conductivities of the solutions of this ternary system, are given in Table 2, while the corresponding specific electrical conductivity isotherms, constructed on the basis of the data given in this table, are shown in Fig. 2. The specific electrical conductivity isotherms of the binary system acetic acid-water, constructed on the data of N. A. Trifonov and S. I. Cherbov [6], is shown below the dotted Line 3.

Pyridine-Acetic Acid-Water System

Many of the properties of the binary system pyridine-acetic acid have also been studied by physicochemical analysis methods. In particular, the fusion method was used by Puschin and Rikovski [3], the viscosity method by Faust [10] and others, and the electrical conductivity method by Petten [11], A. N. Sakhanov [12], N. A. Trifonov and S. I. Cherbov [6], A. S. Naumova [13] and others. The diagrams of these properties indicate the formation of four compounds in the system; however, reliable mention can be made of only two compounds, and specifically: $C_5H_5N \cdot CH_3COOH$ (by the fusion diagram) and $C_5H_5N \cdot 2CH_3COOH$ (by all of the other properties). The specific electrical conductivity isotherm of the system pyridine-acetic acid shows a maximum, found at approximately 80 mole % acetic acid.

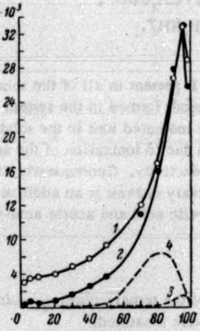

Figure 3. Electrical conductivities of the systems: 1) $C_5H_5N \cdot 2CH_3COOH-H_2O$; 2) $C_5H_5N \cdot CH_3COOH-H_2O$; 3) $CH_3COOH-H_2O$; 4) $C_5H_5N-CH_3COOH$.

TABLE 3

Amount of H_2O (in mole %)	$\varkappa_{20} \cdot 10^3$	
	$C_5H_5N \cdot 2CH_3COOH-H_2O$	$C_5H_5N \cdot 2CH_3COOH-H_2O$
2	0.6126	3.335
5	0.5343	3.703
10	0.7203	3.775
20	0.9793	4.354
30	1.674	4.988
40	2.365	5.758
50	3.675	7.176
60	5.997	9.024
70	11.80	12.067
80	16.29	17.43
90	28.06	27.05
95	33.07	33.09
98	26.46	29.46

For our study we prepared solutions composed of 50 mole % acetic acid and 50 mole % pyridine in water, and 33 mole % acetic acid and 67 mole % pyridine in water.

The results of our specific electrical conductivity measurements are given in Table 3, while the corresponding isotherms are shown in Fig. 3.

DISCUSSION OF RESULTS

As can be seen from the presented plots, the electrical conductivity of the studied solutions shows constant increase in measure with the addition of water to the mixtures of amine and acetic acid; here the specific electrical conductivity passes through a sharp maximum at 95 mole % water and then drops rapidly. Of interest is the fact that all of the solutions of the ternary systems show much greater electrical conductivities than do the solutions of the binary systems, composed of acetic acid and the same amines. Thus, for example, the maximum specific electrical conductivity shown by solutions of the ternary system quinoline-acetic acid-water exceeds $12 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. The maximum electrical conductivity shown by solutions of the binary system quinoline-acetic acid, as can be seen from the presented specific electrical conductivity isotherm (Fig. 1, dotted line), is equal to only $2 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, while the maximum electrical conductivity shown by the system acetic acid-water is even less, being of the order of $1.6 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. An even greater difference in the maximum specific electrical conductivity is observed in the aniline-acetic acid system. Thus, for example, the maximum specific electrical conductivity shown by solutions of the ternary system aniline-acetic acid-water is $32 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, while at the same time the maximum electrical conductivity shown by solutions of the binary system aniline-acetic acid fails to reach $3 \cdot 10^{-3}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. As a result, the addition of water to binary systems, composed of amines and acetic acid, leads to a 7- to 10-fold increase in the electrical conductivity. In isolated cases the specific electrical conductivity shown by solutions of the ternary systems is more than 3 times greater than the electrical conductivity shown by 0.1 N potassium chloride solution. This makes it possible to select the desired solution of the ternary system for running the electrolysis under optimum conditions. Such a large increase in the electrical conductivity shown by solutions of binary systems, composed of amines and acetic acid, when water is added to them, in our opinion, can be explained as follows. The electrical conductivity shown by solutions of binary systems, composed, for example, of aniline and acetic acid, is determined by the ionization of the compounds formed in this system by the following schemes:

$$1)\ C_6H_5NH_2 \cdot 2CH_3COOH \rightleftarrows C_6H_5NH_3^+ + CH_3COOH \cdot CH_3COO^-,$$

$$2)\ C_6H_5NH_2 \cdot CH_3COOH \rightleftarrows CH_3COO^- + C_6H_5NH_3^+.$$

The added water ionizes an additional amount of the acid, which is present in all of the solutions in excess, since all of the binary systems taken by us are irrational, i.e. the compounds formed in the system suffer decomposition into their components. As a result, together with the above indicated ions in the solutions of the ternary systems studied by us, there also appear H_3O^+ and CH_3COO^- ions due to ionization of the acid molecule. Naturally, this should lead to a noticeable increase in the electrical conductivity. Consequently, it can be said that the total electrical conductivity shown by solutions of the above ternary systems is an additive value, based on the electrical conductivities shown by two binary systems: amine-acetic acid and acetic acid-water.

SUMMARY

1. The electrical conductivities shown by a number of solutions of the ternary systems: quinoline-acetic acid-water, aniline-acetic acid-water and pyridine-acetic acid-water were measured.

2. It was established that the electrical conductivities shown by solutions of these ternary systems are always greater than are the electrical conductivities of the corresponding solutions of the binary systems, formed from amines and acetic acid or from acetic acid and water. In individual solutions the addition of water to solutions of the binary systems leads to a 10-fold increase and more in the electrical conductivity. This increase in electrical conductivity is explained by the independent ionization of the acid in water, and of the complex formed by the acid and amine.

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ELECTROLYTIC DISSOCIATION IN NONAQUEOUS SYSTEMS

IV. ANILINE-ALLYL MUSTARD OIL SYSTEM

S. P. Miskidzhyan

A study of electrolytic dissociation in nonaqueous systems is of great practical and theoretical interest.

Of the nonaqueous systems the greatest interest is shown by those that are formed from nonconductive components, while at the same time their solutions show good conductance of an electric current. Several such systems had been studied by us earlier for the purpose of establishing the mechanism of the electrolytic dissociation shown by the compounds formed in them. In one of our published papers [1] we were able to show that in the system piperidine-allyl mustard oil, parallel with the formation of the substituted thiourea, there is also obtained allylpiperidine hydrothiocyanate, which decomposes into its ions. This well explains both the presence of CNS^- ions in the system and the manifestation of considerable electrical conductivity for its solutions.

In connection with the above it is of interest to also make a study of several other analogous systems, composed of allyl mustard oil and other aromatic amines, for the purpose of elucidating whether the mechanism proposed by us for electrolytic dissociation [1] is also general for them.

We selected the system aniline-allyl mustard oil as being such a system. The fusion and viscosity properties of this system have been studied by N. S. Kurnakov and I. Kvyat [2]. Both the viscosity isotherms and the equilibrium diagram agree in showing the formation of allylphenylthiourea in the system – a crystalline substance with m. p. 98.5°. This same system was studied later by N. A. Trifonov and K. I. Samarina [3] by the electrical conductivity method at 100 and 125°. The specific electrical conductivity isotherms obtained by them show two maxima and one minimum, corresponding to the composition of the compound. A minimum on the electrical conductivity isotherm in similar rational systems, as was shown by N. A. Trifonov [4], is the result of a sharp increase in the viscosity of the solutions, corresponding to the composition of the compound formed in the system. When the influence of viscosity was eliminated the above authors obtained a "corrected" electrical conductivity isotherm with a maximum corresponding to 50 mole %.

The electrical conductivity shown by individual solutions of this system at 100° reaches the order of $4.3 \cdot 10^{-3}$, i.e. it is approximately 4 times as great as the electrical conductivity shown by 0.01 N aqueous sodium chloride solution at 20°. This circumstance makes this system of especial interest from the viewpoint of studying the character of the electrolytic dissociation of the compound formed in the system, and appearing as an electrolyte. It is difficult to explain the presence of such a high electrical conductivity if it is assumed that only allylphenylthiourea is formed in the reaction of aniline with allyl mustard oil. As our experiments revealed, together with allylphenylthiourea, the reaction of aniline with allyl mustard oil also results in the formation of another reaction product, which appears as an electrolyte and in the main determines the high electrical conductivity shown by the solutions of the system.

EXPERIMENTAL

We synthesized allyl mustard oil by the method described in the literature [5]. The oil obtained in this manner was dried over calcium chloride and then distilled twice. For our work we took the fraction with b. p. 150-151° at 740 mm; d_4^{20} – 1.069. The aniline was dried by the method of long standing over potassium hydroxide, after which it was distilled. For our work we took the fraction with b. p. 182.7-183.0° at 730 mm.

The gravimetric method was used to prepare the solutions. We failed to observe any appreciable heating up when the components were first mixed, but on standing, in measure with progress of reaction between the components, the mixtures showed strong heating up. At the end of reaction a crystalline substance was present in all of the solutions studied by us (with the exception of 4.9 and 95 mole % of allyl mustard oil). Testing of the prepared solutions for the presence of CNS^- ions (by treatment with ferric chloride solution and other qualitative reactions) enabled us to show their presence in all of the solutions. Pure allyl mustard oil fails to give a coloration with ferric chloride even when heated. The conjecture might arise that the CNS^- ions are formed when either the components of the system or the compounds formed in the system come in contact with the water that is present in the aqueous ferric chloride solution. To check on this postulation we reacted dry ferric chloride with the liquid solutions of our system; here we obtained an evenbrighter red coloration.

We were also able to show the presence of CNS^- ions by electrolyzing the liquid solutions of our system with an iron anode. When a current was passed through the solution the liquid at the iron anode assumed a bright red coloration. As a result, it can be considered undisputed and demonstrated that CNS^- ions are present in the solutions of our studied system. In connection with this it seemed of interest to quantitatively determine the concentration of these ions as a function of the composition of the mixtures in the system. In view of the fact that the mixtures of the given system show comparatively good solubility in ethyl alcohol (even in aqueous alcohol) with the formation of CNS^- ions, we deemed it possible to employ the method recommended by A. K. Babko [6] for the colorimetric determination of CNS^-, taking 90% ethyl alcohol as the solvent. According to the data of the above author, such a solvent makes it possible to determine the CNS^- concentration more accurately than in water, since the instability constant of the complex, which in the main determines the color of the solution, is considerably smaller than in water. We used a photoelectrocolorimeter of native manufacture to determine the concentration of CNS^- ions. To obtain a calibration curve we prepared a number of solutions of c. p. potassium thiocyanate, dried at 120-130°, in 90% ethyl alcohol. The measurements were run in a cuvette with a thickness of 0.45 cm. A No. 2 light filter was used, i.e. with a maximum transmission of 450-500 mμ.

To determine the CNS^- concentration in individual mixtures of the studied system we took a known weight of the mixture and dissolved it in 90% ethyl alcohol. Having added 2 ml of 5% ferric chloride solution and 1 ml of 30% nitric acid, we then brought the total volume up to 100 ml. For convenient comparison we expressed the CNS^- concentration in gram-ions per liter of alcohol solution when 1 g of mixture of variable composition was dissolved in it. The results that we obtained in this manner are shown in the table. The curve, expressing the CNS^- concentration as a function of the composition of the system, is shown in Fig. 1.

Electrical Conductivity and CNS^- Concentration in the System Allyl Mustard Oil-Aniline as a Function of Composition

Amount of allyl mustard oil in the mixture (in mole %)	CNS^- concentration (expressed in normalities when calculated on the basis of 1 g of mixture in 1 liter)	$\kappa_{96} \cdot 10^3$	$\kappa \cdot \eta$
4.90	0.0000505	0.06298	0.0004704
15.47	0.0001295	0.7216	0.007433
29.84	0.0001678	1.0369	0.020950
33.37	0.0001908	1.0322	0.022920
45.37	0.0002742	0.7036	0.041683
50.20	0.0003375	0.5797	0.046433
55.08*	0.0003486	1.2719	0.064486
70.21	0.0003406	2.9004	0.049887
84.97	0.0000639	1.2684	0.007572
94.55	0.0000527	1.08998	0.0043599

* Measured in supercooled state.

As can be seen from the plot, the mixture containing 55 mole % of allyl mustard oil shows the maximum concentration of CNS⁻ ions. We also measured the electrical conductivity of the system aniline-allyl mustard oil. In general, the results that we obtained here support the data obtained by N. A. Trifonov and K. I. Samarina [3]. The results of measuring the specific electrical conductivity at 95° are given in the third column of the table.

If we plot the diagram of corrected electrical conductivity ($\kappa \cdot \eta$) against composition of the mixture, we obtain the curve shown in Fig. 1, from which it can be seen that the corrected electrical conductivity of the solutions in the system changes in unison with the concentration of CNS⁻ ions. This gives basis to assume that the presence of appreciable electrical conductivity for the solutions of the system is determined by the presence of the CNS⁻ anion and complex cation in them.

In the course of our study it was observed that heating of the solutions leads to a change in the concentration of CNS⁻ ions in the mixture. To quantitatively study this phenomenon we subjected some of the solutions prepared by us to prolonged heating at 110-120° and measured the CNS⁻ concentration in them as a function of the duration of heating. In this connection the mixtures showed considerable darkening, which was also observed by N. N. Zinin [7], who was the first to synthesize allylphenylthiourea. The results of these measurements are shown in Fig. 2, from which it can be concluded that the CNS⁻ concentration in the studied mixtures increases under heating and when heated for a sufficiently long time should attain some constant value. This led us to the thought that apparently some substance is formed in the heating, which serves as a source for the formation of CNS⁻ ions in the solutions of the system. This postulation is supported in part by the fact that the mixtures when heated in alcohol solution show a comparatively good conductivity ($\kappa \cdot 10^{-3}$) and with ferric chloride give a positive test for CNS⁻. At the same time neither pure allylphenylthiourea in anhydrous alcohol, nor freshly prepared solutions of this compound in an excess of the components (not subjected to heating), show electrical conductivity or give a positive test for CNS⁻ ions. Thus, for example, an approximately 0.1 N solution of allylphenylthiourea in aniline at 20° shows an electrical conductivity of the order of $2 \cdot 10^{-7}\ \Omega^{-1}\ \mathrm{cm}^{-1}$, in allyl mustard oil $6 \cdot 10^{-6}$, and in anhydrous alcohol $3 \cdot 10^{-6}$. Exactly as our experiments revealed, if the crystalline allylphenylthiourea formed in the system is thoroughly washed free (with ethyl alcohol) of excess components and dried, it fails to conduct a current ($\kappa = 8 \cdot 10^{-7}$) in the molten state (at 100°). All of these solutions fail to give a qualitative test for CNS⁻, with the exception of the solution of allylphenylthiourea in allyl mustard oil, and then only when stored for a long time. As a result, it must be assumed that if only allylphenylthiourea is formed when aniline and allyl mustard oil are mixed, then the solutions of the system should fail to show appreciable electrical conductivity.

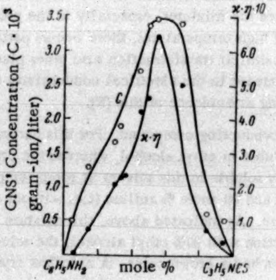


Figure 1. Corrected electrical conductivity ($\kappa \cdot \eta$) and CNS⁻ concentration as a function of composition in the system allyl mustard oil-aniline.

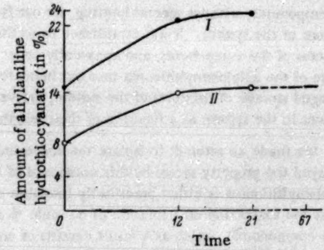
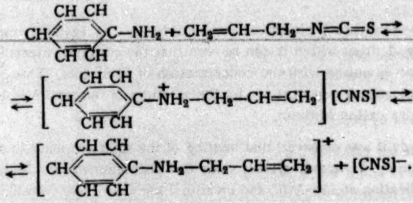


Figure 2. Increase in the amount of allylaniline thiocyanate in the system allyl mustard oil-aniline as a function of the length of heat treatment. I) Mixture containing 70.2 mole % allyl mustard oil, II) the same with a 50.0 mole % content of allyl mustard oil.

Proceeding from the above and some experimental data, which will be described below, we believe that in the reaction of allyl mustard oil with aniline, together with the formation of allylphenylthiourea, the following reaction takes place:



As our experiments show, this reaction proceeds better at a higher temperature; in this connection the temperature, sufficient for this reaction to proceed, shows development under progress of the main reaction for the formation of substituted thioureas. This serves to explain the reason, after termination of reaction between the components, without special heating, for our finding an appreciable concentration of CNS^- ions in the solutions of the system. It was established by us that when we heated the mixtures, especially in the presence of an excess of the components, and apparently under the influence of high temperatures, there occurs partial conversion of the allylphenylthiourea into our indicated compound. A similar transformation also takes place under prolonged storage of mixtures of the system, the very noticeable increase in the electrical conductivity of the solutions in the system as a function of their length of storage serving as evidence of this [8].

We made an attempt to isolate the above-indicated current-conducting compound. For this purpose we employed the property shown by this compound of being readily soluble in ethyl alcohol, whereas the crystalline allylphenylthiourea is either practically insoluble or very difficultly soluble in this solvent at room temperature. We ran the extraction on a mixture of 50 mole % allyl mustard oil and 50 mole % aniline (i.e. without an excess of the components), which as a result consists of only one solid phase. As indicated above, this mixture was heated for a long time, and then, by the method of repeated extraction with 90% ethyl alcohol, the soluble portion of the mixture was extracted. The mixture taken for extraction had a brown color. A colorless crystalline substance (pure allylphenylthiourea) remained after the extraction; the substance extracted by the alcohol had a dark-brown color. Removal of the alcohol by distillation gave a dark-brown oily liquid. When treated with ammonia the liquid solidified into a brown deposit. After filtering this solid substance from the aqueous phase we washed the precipitate with water. We were able to obtain completely pure NH_4CNS crystals when the filtrate was evaporated, which gives basis to assume that the mechanism proposed by us for the secondary chemical reaction is valid.

SUMMARY

The system aniline–allyl mustard oil was studied for the purpose of elucidating the mechanism of electrolytic dissociation shown by the compound formed in it. Together with the formation of allylphenylthiourea, it was established that a secondary reaction also proceeds in the system with the formation of allylaniline hydrothiocyanate, which appears as an electrolyte and serves as a source for the formation of CNS^- ions.

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STUDY OF PHASE EQUILIBRIA IN THE SYSTEM PYRAMIDON-SALICYLIC ACID-WATER

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One of the problems which can be solved by studying three-component systems by the stratification method is a study of chemical reactivity in their binary predominating systems being reflected at the stratification surfaces of the ternary systems. For this purpose nearly always those ternary systems were studied up to now in which a single chemical compound was formed in each of the binary predominating systems, and at the same time the types of geometric elements found at the stratification regions, which reflect this type of reactivity, were elucidated. The question of ternary systems with stratification and with the creation of two chemical compounds in the binary predominating systems was raised in the literature [1], in which connection several theoretically possible forms of the stratification isotherms for such a case were proposed. Of the ternary systems experimentally studied by the stratification method the described form of only one system [2], studied in detail, is known to us, although it was studied for different reasons than in the present work. Nevertheless, a study of this type of system by the stratification method is necessary, and first, for the reason that they are widely encountered among three-component systems possessing practical importance; second, because the character of reflection shown simultaneously by two compounds of a predominating system at the stratification region of a ternary system has failed to receive far from complete study, either experimentally or theoretically. Such a study would greatly expand the theory of liquid phase equilibria and the ramifications of its application. In the present work we studied equilibrium of the liquid phases and, in part, of crystallization in the three-component system pyramidon-salicylic acid-water. On the one hand, this system was selected for the reason that preliminary experiments revealed the formation of two chemical compounds in the binary system pyramidon-salicylic acid. On the other hand, the binary system salicylic acid-water is a system showing stratification [3], which, it is understood, will also be observed in the ternary system. As a result, in the three-component system pyramidon-salicylic acid-water we can expect the reflection of two compounds of a binary predominating system at the stratification region of a ternary system. A study of the character and properties of this reflection is the main purpose of the present work.

EXPERIMENTAL

We took the following substances for our work: pharmacopoeia pyramidon (dimethylaminoantipyrine) with m. p. 108°, c. p. salicylic acid with m. p. 155°, and twice-distilled water. Stratification was studied by the well-known Alekseev polythermal method [4] in sealed glass ampuls in an oil-bath thermostat, while fusion was studied by the visual method, with seeding.

Of the binary systems in the three-component system pyramidon-salicylic acid-water only the system salicyclic acid-water is described in the literature [3]. This system shows a region of metastable equilibrium between the liquid phases with an upper critical solution temperature of 89.1°, corresponding to a composition equal to 32% salicylic acid. The other two binary systems of the given ternary system, pyramidon- salicylic acid and pyramidon-water, were studied in the present work.

The system pyramidon-salicylic acid (P-Sa) was studied by the fusion method. The numerical data obtained here are given in Table 1, while the fusibility diagram is shown in Fig. 1. As Fig. 1 shows, the formation of two compounds is revealed in this system: the compound PSa, melting without decomposition at

97.0° and containing 37.40% salicylic acid and 62.60% pyramidon, in which the pyramidon and salicylic acid molecules are found in a 1:1 ratio; and the compound PSa_3, melting with decomposition at 94.0°, and in which the pyramidon and salicylic acid molecules are found in a 1:3 ratio, representing a content of 64.20% salicylic acid and 35.80% pyramidon. Here the found transition point E corresponds to a temperature of 93.5° and a content of 63% salicylic acid and 37% pyramidon, i.e. it is located close to the concealed m. p. of PSa_3. Two eutectic points are found in this system: point e_1 at 87.0°, corresponding to a composition of 18% salicylic acid, and point e_2 at 82.0°, corresponding to a salicylic acid content of 51.50%. The external appearance and behavior of the described compounds proved to be different. Compound PSa crystallizes as fine short prisms, and shows good seeding by pyramidon and poor seeding by salicylic acid. Compound PSa_3 crystallizes as fine needle crystals, but which are shorter than for salicylic acid; it is easily seeded by the latter, but poorly by pyramidon.

TABLE 1

Equilibria in the System Pyramidon-Salicylic Acid

Crystallization temperature	Amount of salicylic acid (wt. %)	Crystallization temperature	Amount of salicylic acid (wt. %)
82.0°	51.5	96.5°	39.0
83.0	52.0	97.0	35.0
84.0	50.0	97.0	37.4
87.0	18.0	98.0	10.0
88.0	20.0	99.0	64.0
90.0	45.0	103.0	65.0
90.0	55.0	104.0	5.0
91.0	15.0	107.0	66.0
91.0	25.0	108.0	0.0
92.0	43.0	116.0	68.0
93.0	28.0	124 0	70.0
93.0	60.0	134.0	75.0
93.5	63.0	142.0	80.0
94.0	30.0	152.0	90.0
95.0	40.0	155.0	100.0

TABLE 2

Equilibria in the System Pyramidon-Water

Temperature	Amount of H_2O (wt. %)		
	Stratification		crystallization
	layer A	layer B	
169°	60		—
167.5	50	—	—
167	—	70	—
165	40	—	—
160	30	—	—
158	—	80	—
145	25	—	—
143	—	85	—
130	—	90	—
108	—	—	0
106	—	90	—
86	—	—	5
84	25	—	—
83	—	85	—
78	—	—	10
75.5	—	80	—
74	30	—	—
72	—	—	20
71	—	70	30
70.5	—	—	40
70.5	—	—	50
70.5	—	—	60
70.0	—	—	70
69.5	—	—	80
69.0	40	—	—
68.0	50	60	—
68.0	55		—
62.0	—	—	90
15.0	—	—	95

The system pyramidon-water* was studied by both the stratification and fusion methods. The numerical data obtained here are given in Table 2, while the stratification and crystallization polytherms are shown in Fig. 2 by the heavy curves O_s and O_k, respectively. As Fig. 2 shows, the stratification polytherm is a closed curve with two critical solution points, K_1 and K_2. The lower critical solution point K_1 corresponds to a temperature of 68.0° and a water content of 55%. The upper critical solution point K_2 corresponds to 169.0° and 60% water. Consequently, the two critical points fail to be found on the same vertical. Along the median temperatures between the critical points the solubility of the components in each other remains practically constant for quite a long temperature interval. Thus, the solubility of liquid pyramidon in water from 90 to 135° remains equal to 10%, while the solubility of water in liquid pyramidon remains constant from 80 to 155°, and is equal to 24%. In contrast, near the critical points the mutual solubility of the liquid phases strongly depends on the temperature, and here portions of the curve are very sloping. As a result of this the plane of the two-phase liquid state, bounded by curve O_s, shows an angular character and stretches from 68 to 169°, and in a concentration interval of 24 to 90% water.

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* With participation by E. N. Korobenko.

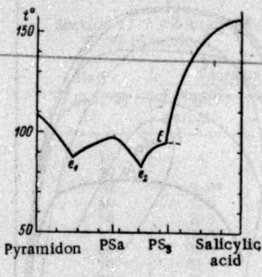

Figure 1. Fusion diagram of the system pyramidon-salicylic acid.

On the diagram of the binary system pyramidon-water the straight line ab is at the same time also a portion of the crystallization curve and a conode of the stratification region; consequently, monotectic equilibrium is realized on this straight line, lying at 70.5°. It can be expressed by the equation for the reversible reaction $a \rightleftharpoons b + P$, where a is a saturated solution of water in pyramidon at 70.5°, and b is a saturated solution of pyramidon in water at the same temperature; solution a contains 65% pyramidon, and solution b contains 32% of the latter. When the temperature is lowered solution a vanishes (decomposes), and the pyramidon will be found in equilibrium with the saturated solution. When the temperature is raised the solid pyramidon phase vanishes (dissolves), and two liquid phases will be found in stable equilibrium.

At a temperature of approximately 70° the pyramidon crystallization curve O_k shows a long, nearly horizontal portion over an extent of 55% (from 25 to 80% water), which is considerably longer than the monotectic equilibrium portion ab. As was shown earlier [5], similar sloping portions on crystallization curves indicate the presence in the systems of metastable equilibrium between liquid phases. As Fig. 2 shows, this actually happens in the mixtures with compositions between a and b, at temperatures ranging from the lower critical point to 70.5°; consequently, the lower critical solution point K_1 is also metastable. This last fact is extremely important, since only a single binary system is known in the literature, methyl iodide-pyridine [6] in which metastable equilibrium exists between liquid phases with a lower critical solution temperature. In this system methyl iodide and pyridine react with each other to form a chemical compound with a component ratio of 1 : 1. The minimum of the stratification curve is found below the crystallization curve of this compound, i.e. here we have a complicated case of this type of binary system. Stable chemical compounds fail to be formed in the system pyramidon-water; here only hydration is possible, and the minimum of the stratification curve is found below the crystallization curve for pyramidon, i.e. one of the components. As a result, the pyramidon-water system is the first of the simpler cases of this type of binary system.

In summary, a study of the binary systems of the investigated ternary system reveals that two of them are formed with water present and with stratification, while the third system, pyramidon-salicylic acid, results in the formation of definite chemical compounds, and consequently, the last will be the predominating system in the three-component system pyramidon-salicylic acid-water.

To study the ternary system pyramidon-salicylic acid-water we studied the polythermal sections through its composition prism, going from the water ridge to the side of the binary system pyramidon-salicylic acid. We studied a total of ten such sections with a salicylic acid content of 0.4, 1, 5, 10, 40, 45, 54.5, 64.2, 80 and 90%, assigning numbers to these sections commensurate with increase in the percent of salicylic acid. The numerical material obtained here for the sections is given in Table 3. The absence of sections in the concentration interval from 10 to 40% salicylic acid is because preliminary experiments revealed the absence of stratification in the ternary system within this concentration interval. In the latter is found that section of the ternary system that falls in the binary system pyramidon-salicylic acid on the composition of the compound PSa, present, as will be shown below, in the liquid phase. In the ternary system pyramidon-salicylic acid-water this section, water-compound PSa, plays the role of a quasibinary section; it divides the whole ternary system into two quasiternary systems: water-pyramidon-compound PSa and water-compound PSa-salicylic acid. As a result, it proved necessary to subdivide the polytherms of all of the sections into two groups, for which reason they are shown on two plots: the polytherms of those sections (1-4) that are located in the quasiternary system water-pyramidon-compound PSa are shown in Fig. 2, while the polytherms of the sections (5-10) that are located in the quasiternary system water-compound PSa-salicylic acid are shown in Fig. 3.

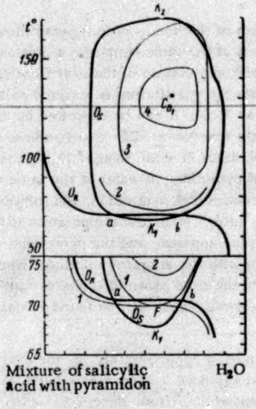

Figure 2. Equilibria of solid and liquid phases in the system pyramidon-water (heavy lines) and polytherms of the ternary system pyramidon-salicylic acid-water close to this binary system (fine lines). Beneath is given the lower tangential portion of the diagram under magnification.
Explanation in the text.

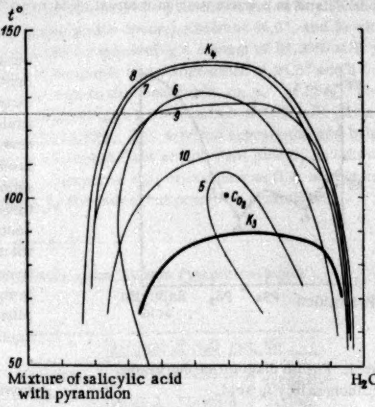

Figure 3. Polytherms of the ternary system pyramidon-salicylic acid-water, adjacent to the binary system salicylic acid-water (the latter is shown by the heavy line).
Explanation in the text.

In the quasiternary system water-pyramidon-compound PSa the chemical compound PSa functions to homogenize stratification in the binary system pyramidon-water. As a result of this, as Fig. 2 shows, the stratification polytherms of Sections 1-4 appear as closed curves, similar to the stratification curve of the binary pyramidon-water system. These curves show concentric diminution in measure with increase in the PSa content in the sections and consequently, in the final end, converge into point C_{0_1}, which can be named a ternary point of solubility change. • It corresponds to a temperature of 130° and the composition: 65% water, 30% pyramidon, and 5% salicylic acid.

The described portion of the equilibrium diagram of the above ternary system is characterized by the fact that here elevation of the temperature results in transition of the metastable equilibrium between the liquid phases into the stable form. Similar transitions have been studied for systems showing upper critical solution temperatures [7]. For systems with lower critical solution temperatures such transitions are completely unknown, and they have been realized here for the first time. In the study [7] it was shown that it is necessary for such transitions to pass through a section at a tangent and with a tangential point, for which reason they were found for the ternary system pyramidon-salicylic acid-water. The lower part of the curves, where the indicated geometric elements are located, is shown under magnification of the temperature scale in the lower part of Fig. 2.

• Similar points of binary systems can be named binary points of solubility change. This is associated with the situation that in raising the temperature the solubility of one component in another decreases up to this point, and shows increase after it. In the general case the indicated binary and ternary points of the same stratification surface fail to be found at the same temperature, although in principle this is possible. At times, instead of points, intervals are realized.

TABLE 3

Equilibria in the System Pyramidon-Salicylic Acid-Water

Section 1: 0.4% salicylic acid, 99.6% pyramidon

Water (wt. %)	Temperature	
	of stratification	of crystallization
10	—	77.0°
20	—	71.0
30	80.0°	70.5
40	72.0	70.0
50	70.0	70.0
55	70.0	70.0
60	70.0	70.0
70	41.5	69.5
80	76.0	68.5
90	—	61.0

Section 2: 1.0% salicylic acid, 99% pyramidon

Water (wt. %)	Stratification temperature
30	85.0°
40	77.0
50	74.0
60	73.0
70	74.0
80	81.0

Section 3: 5% salicylic acid, 95% pyramidon

Water (wt. %)	Stratification temperature	
	upper	lower
40	133.5°	99.0°
50	157.0	92.5
60	163.0	89.0
70	167.0	88.0
80	161.0	93.0
82	155.0	100.0

Section 4: 10% salicylic acid, 90% pyramidon

Water (wt. %)	Stratification temperature	
	upper	lower
50	133.0°	120.0°
60	143.0	116.0
70	144.0	114.0
75	144.0	114.0
77	140.0	116.0

Section 5: 40% salicylic acid, 60% pyramidon

55	103.5°	95.0°
60	107.5	82.0
70	97.0	66.0
80	80.0	—

Section 6: 45% salicylic acid, 55% pyramidon

28	100.0°	80.0°
30	110.0	72.0
35	120.0	55.0
40	126.0	39.0
50	129.5	—
60	129.0	—
70	124.0	—
80	108.0	—
85	95.0	—
90	77.0	—

Section 7: 54.5% salicylic acid, 45.5% pyramidon

Water (wt. %)	Stratification temperature
20	85.0°
23	110.0
30	128.0
40	136.0

Section 8: 64.2% salicylic acid, 35.8% pyramidon

Water (wt. %)	Stratification temperature
17	70.0°
20	105.5
30	130.0
40	137.0

(Continued)

TABLE 3 (Continued)

Water (wt. %)	Stratification temperature
50	137.5°
60	137.5
70	136.0
80	125.0
90	98.0
95	70.0

Water (wt. %)	Stratification temperature
50	138.5°
55	138.5
60	138.5
70	137.0
80	128.5
90	108.0
95	89.0
97	65.0

Section 9: 80% salicylic acid, 20% pyramidon

20	80.0°
30	115.0
40	125.0
50	126.5
60	127.0
70	127.0
80	123.0
90	105.0
95	80.0
96	70.0

Section 10: 90% salicylic acid, 10% pyramidon

25	69.0°
30	92.0
40	105.0
50	110.0
60	113.0
70	113.0
80	112.0
85	110.0
90	101.0
95	75.0

As Figure 2 indicates, the section showing the tangency is the first section with a salicylic acid content of 0.4%. In this section the system, corresponding to the tangential point F, contains 55% water and corresponds to a temperature of 70°; the curve for the crystallization of pyramidon was also determined in it. Stable stratification is realized at temperatures above point F; consequently, this tangential point differs sharply from that seen in the transitions with upper critical temperatures. At the tangential point F, in view of the identity in the composition of the two liquid phases, the system will be found in univariant equilibrium. At point F the crystallization curve and the stratification curve possess a common tangent.

An upper ternary critical point is realized in the quasiternary system water-compound PSa-salicylic acid. Its presence is already indicated by the character of the sections in this portion of the diagram, shown in Fig. 3. From Sections 5 to 8, the maximum points of their polytherms increase, and from Sections 8 to 10 they decrease; consequently, the polytherm of Section 8 is the highest. The maximum point of this section represents the upper ternary critical solution point K_4; it corresponds to 138.5° and a composition of 55% water, 29% salicylic acid and 16% pyramidon. Section 8 in the binary system pyramidon-salicylic acid falls on the composition of the second compound PSa_3. Consequently, the presence of compound PSa_3 in the liquid phase of the ternary system and its predominating binary system establishes the ternary critical solution point.

In the quasiternary system water-compound PSa-salicylic acid the compound PSa serves to effect homogenization of the stratification found in the binary system salicylic acid-water. The homogenizing properties of compound PSa, appearing in the two above-described liquid quasiternary systems, in its influence on the character and form of their stratification surfaces, indicates the presence of this very same chemical compound in the liquid phase of the ternary system and its predominating binary system, despite the complete homogeneity shown by the section water-compound PSa. Consequently, establishing the presence of this compound in the liquid phase on the basis of its homogenizing properties is fully valid. The fact that the presence of this same compound in the same concentration interval is also shown by the fusion method makes it that much more valid. To this must be added the fact that a number of studies are known in the literature on the homogenizing properties shown by binary systems [8], in which connection the chemistry prevailing in these systems is determined specifically by these properties. Despite this, establishing the presence of a single individual substance in the liquid phase on the basis of its homogenizing properties is done here for the first time.

As Fig. 3 shows, in all of the sections the solubility of water in the liquid pyramidon-salicylic acid mixtures is considerably greater than is the solubility of these mixtures in water; in this connection the mutual solubility of the liquid phases shows an increase in most of the sections when the temperature is raised. In view of this most of the polytherms in their form are similar to the stratification curve of the binary system salicylic acid-water, shown in Fig. 3 by a heavy line with critical point K_3. Near the edges the mutual solubility polytherms of the liquid phases depend but slightly on the temperature, and they rise sharply upward, while close to the mixing temperatures this dependence is strong and portions of the polytherms are sloping. However, in

Sections 5 and 6, situated close to the section based on the composition of compound PSa, the branches of the polytherms, expressing the solubility of water in the liquid pyramidon-salicylic acid mixtures, show portions in which this solubility decreases with temperature elevation. At the same time the region bounded by the solubility polytherms shows a strong decrease from Section 8 to 5. Both of these characteristics of the sections suggest that a ternary point of solubility change C_{0_2}, located toward the side of the quasibinary section water-compound PSa, is realized at the stratification surface of the quasiternary system water-compound PSa – salicylic acid. This point corresponds to ~100° and a composition of 60% water, 16% salicylic acid and 24% pyramidon.

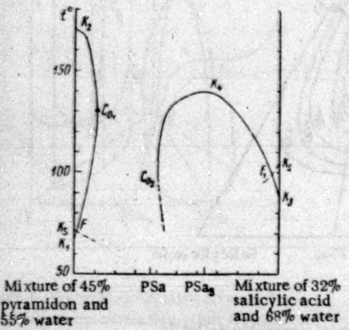

Figure 4. Projection of the curves through the characteristic points of the stratification surfaces in the system pyramidon-salicylic acid-water on the side of the pyramidon-salicylic acid system.

In the binary system salicylic acid-water there is present metastable equilibrium between the liquid phases with an upper critical solution temperature, which becomes stable in the transition to the ternary system. Such transitions of metastable liquid-phase equilibria into stable forms in systems with upper critical temperatures, as was indicated, have already been studied [7], for which reason in this portion of the diagram of the studied ternary system attempts were not made to find the tangential point, and it is qualitatively designated in Fig. 4 by point F_1. It is only necessary to mention that here one of the forms of such transitions is realized, namely, transition through the upper ternary critical point.

In the diagram of the ternary system pyramidon-salicylic acid-water two curves were drawn through all of the critical points, tangential points and points of solubility change. The projection of these two lines on the side of the binary system pyramidon-salicylic acid is shown in Fig. 4. In this plot the points K_5 designate the melting points of the mixtures, 104° in the salicylic acid-water system above the upper critical point, and 70.5° in the pyramidon-water system above the lower critical point, i.e. the temperature of monotectic equilibrium. From these points the course of the crystallization curves in the section is qualitatively designated by dotted lines, running parallel to the side of the binary system pyramidon-salicylic acid. In this section the indicated lines embrace all of the characteristic points of the ternary system, for which reason their mutual distribution on its stratification surfaces is clearly and quantitatively shown. In addition, this section gives a clear quantitative representation of the mutual polythermal distribution of both stratification surfaces with respect to each other.

From the experimentally obtained polytherms we constructed the mutual solubility isotherms of the liquid phases in the ternary system pyramidon-salicylic acid-water, which are shown in Fig. 5. In view of the fact that in its temperature the critical point K_4 lies between K_1 and K_2, it follows that the same isothermal sections, found below point K_4, intersect both stratification surfaces. On the strength of this all of the isotherms are situated at a lower temperature than is point K_4, i.e., below 138.5°. Two isotherms at 120 and 135° were constructed for the stratification surface, adjacent to the side of the binary system pyramidon-water. These isotherms fail to show any special points and delineate a very narrow region of heterogeneous mixtures, which indicates very strong homogenization of the stratification shown by the binary system pyramidon-water in the ternary system. For the stratification surface adjacent to the side of the binary system salicylic acid-water five isotherms were constructed at 15, 110, 120, 130 and 135°. They all lie above the critical point K_3 of the binary system salicylic acid-water, with the exception of the first isotherm at 85°, which is situated below this temperature. These isotherms (other than the first at 85°) represent closed curves, showing concentric diminution with temperature elevation. As a result, they converge in the final end into the upper ternary critical point K_4, lying in the section which in the binary system pyramidon-salicylic acid falls on the composition of compound PSa_3. All of the isotherms show mutual solubility minima for the liquid phases that lie in this section, based on compound PSa_3. Consequently, these minima and the upper ternary critical point simultaneously establish the fact that a chemical compound of composition PSa_3 is formed and is present in the liquid phase of both the binary system pyramidon-salicylic acid and the ternary system.

In Fig. 5, together with the isotherms, is shown the projection of the critical line on the composition triangle, passing through the critical points K_3 and K_4 and the polytherm maxima, and appearing as the curve K_3K_4. As Fig. 5 shows, it possesses an inflection point, coinciding with the upper ternary critical point K_4. As a result,

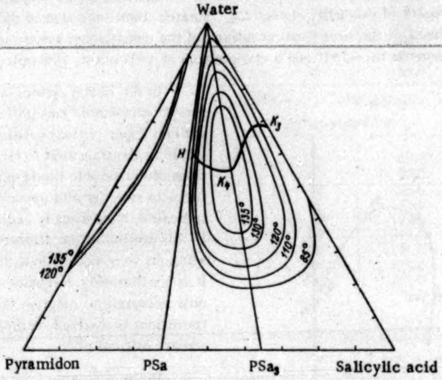

Figure 5. Solubility isotherms of the system pyramidon-salicylic acid-water. The curve K_3K_4H is a projection of the critical line on the composition triangle.
Explanation in the text.

here the important fact is established of the stratification surface of a ternary system being reflected on the critical line by the formation of a chemical compound in the binary predominating system.

In the stable state both the binary system salicylic acid-water and the section water-compound PSa are homogeneous. Despite this, in the quasiternary system water-compound PSa-salicylic acid a region of specifically stable equilibrium between the liquid phases is realized. This is explained, not by the simple geometric continuation of the region of metastable stratification shown by the binary system salicylic acid-water in the ternary system, but, as has been shown [9], by the fact that systems showing metastable stratification can behave like those with stable equilibrium between the liquid phases. Here it must be borne in mind that this explanation is not associated with the question of the reasons for the origin of the upper ternary critical point and remains in strength even in its absence, this being the situation in the investigated systems [7].

The general qualitative form of the temperature-concentration prism, valid for the ternary system pyramidon-salicylic acid-water, is shown in Fig. 6, where the letters in the angles of the prism are the initials of the components in the system. In Fig. 6, on the one hand, the relationship existing between the character of the binary systems with liquid-phase equilibrium and the character of their adjacent stratification volumes can be clearly seen. On the other hand, the mutual distribution of the stratification volumes themselves and their geometric elements, i.e. the characteristic lines and points, is quite evident.

In the binary predominating system pyramidon-salicylic acid there occurs salt-formation between pyramidon, as the base, and salicylic acid: two salts having the composition PSa and PSa_3 are formed. As Fig. 5 shows, the behavior of these salts toward the third component, water, playing the role of solvent, i.e. the character of their individual reaction with it, is directly opposite. The compound having the composition PSa shows unlimited solubility in water and by its homogenizing properties, as was discussed above, shows its presence in the liquid phase. Consequently, the compound PSa reacts vigorously with water in the same manner as with a very polar solvent (the dipole moment of the water molecule is $1.84 \cdot 10^{18}$ [10]),shows hydration, and in the liquid phase

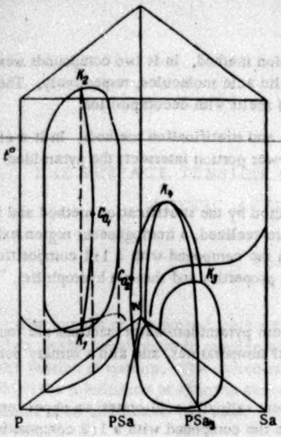

Figure 6. General qualitative form of the temperature-concentration prism for the system pyramidon (P)-salicylic acid (Sa)-water (W).
Explanation in the text.

is stabilized by these hydrational processes. As a result, the compound PSa bears a hydrational character, i.e. it possesses hydrophilic properties. Due to these properties the compound PSa divides the stratification surface of the ternary system into two portions of a homogeneous region. In contrast, the compound with composition PSa_3 shows limited solubility in water, suffers stratification with it, and is established in the liquid phase specifically by the minima on the solubility curves of the liquid phases, together with the upper ternary critical point. Consequently, the compound PSa_3 fails to be stabilized by hydrational processes, but instead by association processes. As a result, the compound PSa_3 bears an associational character and possesses hydrophobic properties.

A sharp change in the properties shown by mixtures of a binary system in direct contrast to the change in the concentration of the components in the system is not astonishing; it has been encountered earlier in physico-chemical analysis. Thus, for example, in the binary system silicon dioxide-magnesium oxide, studied by V. D. Nikitin [11], the phenomenon of stratification of the liquids is observed in the concentration limits of 2 to 29% magnesium oxide, i.e. a weakening of interaction between the components, while at a concentration of 57% magnesium oxide a stable chemical compound, forsterite having the composition $MgSiO_4$, is formed in the system, with a sharp maximum on the fusion diagram. A similar picture of such equilibria is also found quite extensively among other binary systems, formed by the interaction of silica with metal oxides.

The reason for the different and even contradictory properties shown by the two above-described compounds, composed of the same constituents, should undoubtedly lie in the different structure possessed by these compounds, found in continuous association with the medium, and in mutual interrelationship with the solvent. With some basis it can be assumed that in the formation of compound PSa a part of the functional groups of the components remains unbound, appears free in the compound PSa, and determines its strong hydration and unlimited solubility in water. In the formation of compound PSa_3 association proceeds in such manner that here the functional groups are bound, which excludes or makes their hydration highly difficult, and strongly reduces the solubility of this compound in water. As a result, for each of the described compounds a different form of interaction with the solvent is realized, being reflected differently at the stratification surface of the ternary system. The studied system shows that a study of ternary systems by the stratification method permits determining not only the presence and properties of chemical compounds, formed in binary predominating systems, but in a number of cases also permits making certain fundamental decisions relative to their structure.

From the presented material it can be seen, on the one hand, that the form of the stratification surface appears as the result of interaction, both in the binary predominating system and between it and the third component; and on the other hand, that in ternary systems with two chemical compounds in the predominating system the stratification surface fails to be additively composed of two identical geometric elements. Each compound by its properties, interrelationships with the other compound and components of the predominating system, and also with the third component, enters its own characteristic traits into the general picture of liquid-phase equilibria, and as a result of this introduces specific characteristics in the form of the stratification surface. This should also apply to systems with a greater number of components and compounds among them.

SUMMARY

1. The system pyramidon-salicylic acid was studied by the fusion method. In it two compounds were shown with a ratio of 1:1 and 1:3 between the pyramidon and salicylic acid molecules, respectively. The first of these compounds melts without decomposition, and the second melts with decomposition.

2. The system pyramidon-water was studied by both the fusion and stratification methods. In it a closed stratification curve with two critical points was shown, which in its lower portion intersects the pyramidon crystallization curve, with realization of monotectic equilibrium.

3. The ternary system pyramidon-salicylic acid-water was studied by the stratification method and in part by the fusion method. In it two separate stratification surfaces are realized; a homogeneous region exists between them, through which passes the section of the prism based on the compound with a 1:1 composition. This compound is manifested in the liquid phase by its homogenizing properties and shows a hydrophilic character.

4. At the stratification surface adjacent to the side of the system pyramidon-water sections are found showing tangency and a tangential point for the cases of lower critical temperatures, and also a ternary point of solubility change.

5. At the stratification surface adjacent to the side of the system salicylic acid-water an upper ternary critical point is manifested, lying in the section of the prism based on the compound with a 1:3 composition and possessing a hydrophobic character, and also a ternary point of solubility change. This compound is also fixed by the inflection point of the critical line.

6. It was shown that in a number of cases the use of the stratification study method permits judging as to the structure of the compounds that are formed in systems. It was elucidated that in ternary systems with two chemical compounds the stratification surface fails to consist of two identical portions, and instead, each compound is specifically reflected on it. It was also shown that the stratification surface of a ternary system is the result of interaction, both in the predominating system and between it and the third component.

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THE SURFACE TENSION OF BINARY SYSTEMS FORMED BY UREA WITH ACETIC ACID AND ITS CHLORO DERIVATIVES

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The purpose of the present work was to study the interaction of urea with acetic acid and its chloro derivatives in the liquid phase in order to elucidate the relationship that exists between the composition and the surface tension of systems. The choice of components was determined by the desire to establish the manner in which the substitution of chlorine atoms for the hydrogen atoms in the acetic acid radical influences the character of its interaction with urea.

Urea forms compounds with acetic acid and its chloro derivatives, which appear as maxima on the fusion diagrams. A number of investigators [1-4] have very definitely established the presence of the compound $CO(NH_2)_2 \cdot 2CH_3COOH$, in the system urea-acetic acid, which already shows quite strong dissociation at the melting point. According to the data of [5], the presence of the considerably dissociated compound $CO(NH_2)_2 \cdot 2CH_2ClCOOH$, was established in the system urea-monochloroacetic acid. Based on more accurate data obtained later [6], it was established that the two strongly dissociated compounds, $CO(NH_2)_2 \cdot 2CH_2ClCOOH$ and $CO(NH_2)_2 \cdot CH_2ClCOOH$, are present in the fusion diagram of this system.

Two strongly dissociated compounds, $CO(NH_2)_2 \cdot 2CHCl_2COOH$ and $CO(NH_2)_2 \cdot CHCl_2COOH$, also show distinct appearance in the system urea-dichloroacetic acid [6].

The presence of only one compound, $CO(NH)_2 \cdot CCl_3COOH$ [6], was established in the fusion diagram of the system urea-trichloroacetic acid.

To study the surface tension we used the method of the highest pressure shown by a gas bubble [7]. The vessel in which the determinations were made was of the closed type. Mercury served as the sealing liquid (between the cover with a capillary end and the vessel). A screw arrangement was used to lower the capillary end. The pressure was read on a toluene-filled manometer. The temperature was maintained constant to $\pm 0.1°$ by means of a mercury-toluene temperature regulator.

The surface tension was expressed in dynes/cm, and the concentration in mole %.

Prior to use the starting substances were first purified: the acetic acid by freezing, and the urea by repeated recrystallization from water. The monochloroacetic, dichloroacetic and trichloroacetic acids were purified by a double distillation.

The experimental data for the surface tension determinations are given in Tables 1-4. The surface tension curves for urea with acetic acid and its chloro derivatives are shown in Figs. 1-4. The fusion diagrams shown in these plots are based on the data of the studies [4, 6].

As can be seen from the plots, the surface tension smoothly increases with increase in the urea concentration.

The surface tension isotherms in the system urea-acetic acid are convex to the composition axis, which indicates dissociation of the associated compound. The electroconductivity and viscosity curves [6, 8] also indicate the presence of chemical interaction in the system. It can be assumed that the compound $CO(NH_2)_2 \cdot 2CH_3COOH$, already strongly dissociated at the melting point, is completely dissociated in the liquid phase.

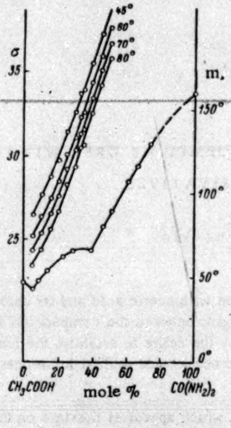

Figure 1. Fusion diagram and surface tension isotherms in the system urea-acetic acid.

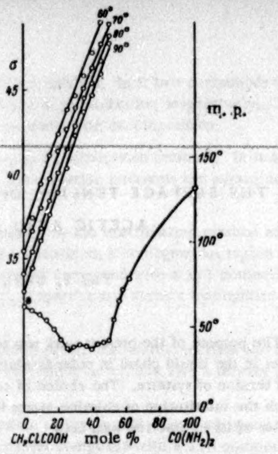

Figure 2. Fusion diagram and surface tension isotherms in the system urea-monochloroacetic acid.

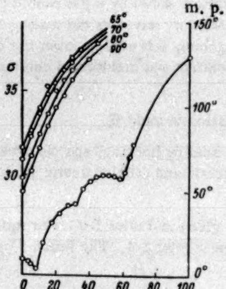

Figure 3. Fusion diagram and surface tension isotherms in the system urea-dichloroacetic acid.

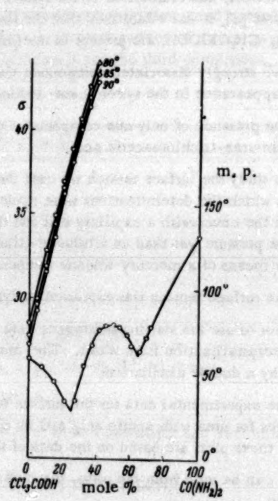

Figure 4. Fusion diagram and surface tension isotherms in the system urea-trichloroacetic acid.

TABLE 1

Surface Tension in the System Urea-Acetic Acid

CH_3COOH (mole %)	Surface tension			
	45°	60°	70°	80°
95	26.65	25.31	24.40	23.51
90	27.79	26.39	25.40	24.41
85	28.91	27.60	26.61	25.70
80	29.85	28.55	27.70	26.80
75	31.56	30.19	29.35	28.41
70	32.74	31.27	30.41	29.43
67	33.92	32.41	31.43	30.60
65	34.07	32.74	31.71	30.78
60	35.69	34.51	33.61	32.71
55	37.46	36.13	35.26	34.39
50	—	37.80	36.88	35.99

TABLE 2

Surface Tension in the System Urea-Monochloroacetic Acid

$CH_2ClCOOH$ (mole %)	Surface tension			
	60°	70°	80°	90°
100.0	36.72	35.40	34.00	32.98
92.35	37.40	36.61	35.36	34.34
85.12	39.44	38.03	36.72	36.04
78.25	41.14	39.80	38.42	37.57
72.03	42.43	41.40	40.12	38.93
65.58	43.86	42.71	41.48	40.29
59.71	44.71	43.90	42.84	42.33
54.26	45.90	45.10	44.54	43.69
48.83	47.26	46.31	45.39	44.71
43.69	48.96	47.71	46.75	45.90
38.84	—	48.93	48.28	47.94
34.17	—	—	—	49.30

TABLE 3

Surface Tension in the System Urea-Dichloroacetic Acid

$CHCl_2COOH$ (mole %)	Surface tension			
	65°	70°	80°	90°
100.00	31.62	30.94	29.75	29.07
89.84	32.64	32.30	31.11	30.26
80.74	34.00	33.70	32.47	31.62
72.50	35.16	34.85	33.66	32.98
65.05	35.91	35.44	35.06	34.00
58.26	36.69	36.42	35.70	34.68
52.05	37.06	36.72	36.30	35.78
46.35	37.40	37.40	—	—
41.10	38.00	—	—	37.02

TABLE 4

Surface Tension in the System Urea-Trichloroacetic Acid.

CCl_3COOH (mole %)	Surface tension		
	80°	85°	90°
100.00	28.54	27.80	27.30
87.47	29.97	29.64	29.30
76.77	32.80	31.96	31.63
67.53	34.96	34.46	33.63
59.48	36.96	36.63	36.30
52.41	38.96	—	38.30
46.13	40.63	40.52	39.96
40.53	42.62	41.36	41.16
35.51	43.96	43.29	42.85
30.96	45.45	45.11	—

It is known [9] that the introduction of chlorine into the acetic acid radical increases its acidity. This should lead to increase in the chemical interaction of urea with the chloro derivatives of acetic acid. However, in our case the surface tension isotherms of all of the systems formed by urea with the chloro derivatives of acetic acid show smooth change with increase in the urea content and fail to give characteristic breaks, which could be associated with the formation of compounds and their stability in a homogeneous molten medium.

SUMMARY

The surface tension isotherms in the systems composed of urea with acetic acid and its chloro derivatives indicate the absence of chemical interaction between the components in the liquid phase.

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THE REACTION OF ETHANOLAMINE WITH DIATOMIC PHENOLS

D. E. Dionisyev and M. G. Kosareva

In a previous study [1] it had been shown that ethanolamine shows chemical reaction with phenol, both in the liquid and in the solid phase. However, in the solid phase a compound with the composition 1 : 2 (2 molecules of phenol) was formed, while in the liquid phase the presence of a compound with an equimolar composition was established.

To establish the influence shown by a second hydroxyl group, introduced in the phenol molecule in the ortho-, meta- and para-positions, we studied the systems formed by ethanolamine with pyrocatechol, resorcinol and hydroquinone. We studied the fusion, density, viscosity and electroconductivity of the indicated systems, which have not been studied before. For our work we used pure ethanolamine of native manufacture, which was distilled after being dried over solid KOH. We took the fraction with b.p. 170.5-171°; m.p. 10°; d^{20}_4 1.020. After recrystallization from water the pyrocatechol of c.p. quality had m.p. 105°. After recrystallization from water the resorcinol of the same quality had m.p. 110°, and the hydroquinone a m.p. of 172°. The method of operation was the same as in previous studies [2]. The density, viscosity and electroconductivity measurements were run at three temperatures. The concentrations were calculated in mole percents, and the viscosity in centipoises.

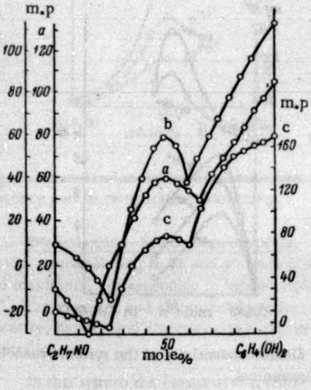

Fig. 1. Fusion of the binary systems of ethanolamine with pyrocatechol (a), resorcinol (b) and hydroquinone (c).

Ethanolamine-pyrocatechol system. The measurement results for the fusion of this system are plotted in Fig. 1 (Curve a). The reaction of ethanolamine with pyrocatechol yields the compound of composition $HOCH_2CH_2NH_2 \cdot o\text{-}C_6H_4(OH)_2$, showing a maximum on the fusion curve at 50 mole % ethanolamine and m.p. 60°, and also two eutectic points (at −9° and 85 mole % ethanolamine, and at 50° and 35 mole % ethanolamine).

The viscosity, density and electroconductivity of the given system were studied at 70, 80 and 90°. We failed to run complete isotherms at these temperatures due to crystallization of the pyrocatechol.

The isotherms of the viscosity η, density d and the temperature coefficient of the viscosity γ are shown in Fig. 2, while the electroconductivity κ and the electroconductivity $\kappa\eta$, corrected for viscosity, are shown in Fig. 3. The isotherms of the viscosity form a maximum at 50 mole %, which with elevation of the temperature is shifted but slightly toward the more viscous component—pyrocatechol (since the η110° of pyrocatechol is 2.00 centipoises, while the η110° of ethanolamine is 1.57 centipoises). On the portion of the curve from ethanolamine to the maximum point the viscosity isotherms are slightly convex to the composition axis, which indicates some association of the ethanolamine.

The curve for the temperature coefficient of the viscosity repeats the course of the viscosity isotherms, and its maximum is also found at 50 mole % of the components.

The presence of maxima on the curves of the viscosity and temperature coefficient of the viscosity, found at an equimolar ratio of the components, indicates that the compound, shown by the fusion method to have a 1:1 composition, is stable in the liquid phase.

The density isotherms appear as curves that are slightly concave to the composition axis.

The electroconductivity isotherms (Fig. 3) show maxima at 70 mole % ethanolamine. "Correction" of the electroconductivity for viscosity fails to change the course of the curve, but here the maximum is more sharply expressed and is found at 50 mole % ethanolamine.

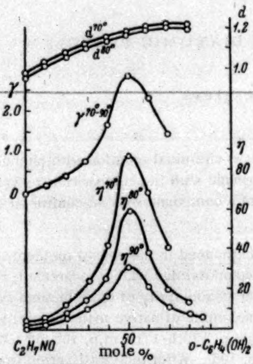

Fig. 2. Ethanolamine-pyrocatechol system: density, viscosity and its temperature coefficient.

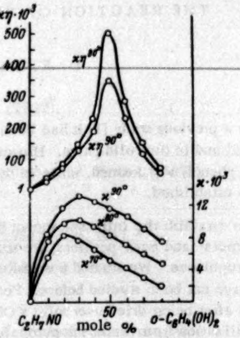

Fig. 3. Electroconductivity of the system ethanolamine-pyrocatechol.

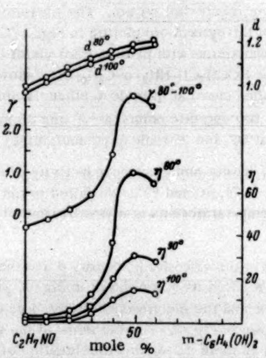

Fig. 4. Ethanolamine-resorcinol system: density, viscosity and its temperature coefficient.

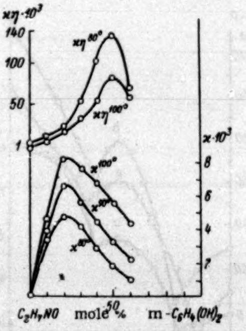

Fig. 5. Electroconductivity of the system ethanolamine-resorcinol.

Ethanolamine-resorcinol system. The study results for the fusion of this system are plotted in Fig. 1 (Curve b), its viscosity and density data in Fig. 4, and its electroconductivity in Fig. 5.

The fusion curve has a maximum with m.p. 60° which corresponds to 50 mole % ethanolamine, and two eutectic points: at 75 mole % ethanolamine (m.p.– 15°) and at 40 mole % ethanolamine (m.p. 38°). Consequently, in the solid phase between ethanolamine and resorcinol a compound of equimolar composition is formed.

The density isotherms at 80 and 100° appear as curves that are slightly concave to the composition axis.

The viscosity isotherms at 80, 90 and 100° appear as curves with a maximum in the region of 50 mole % ethanolamine. As in the preceding system, on that portion of the curve between the ethanolamine side and the maximum the isotherms are slightly convex to the composition axis, which also indicates some association of the ethanolamine.

It should be mentioned that when mixtures containing 70 mole % and more of ethanolamine are heated to 80° and higher, they turn brown and viscous, in which connection the evolution of individual gas bubbles is observed. For this reason the density, viscosity and electroconductivity of the system were studied only up to 60 mole % resorcinol. The mixtures rich in resorcinol show marked darkening and decomposition when kept in the thermostat for a long time. The curve for the temperature coefficient of the viscosity repeats the course of the viscosity isotherms, and its maximum also corresponds to 50 mole % ethanolamine.

The shape of the electroconductivity curve (Fig. 5) is similar to that of the ethanolamine-pyrocatechol system, only here the maximum is found at 80 mole % ethanolamine. When the electroconductivity is corrected for viscosity the maximum is retained, but is expressed more sharply and corresponds to 50 mole % ethanolamine.

On the basis of the obtained results it can be concluded that the compound, shown by the fusion method, also exists in the liquid phase.

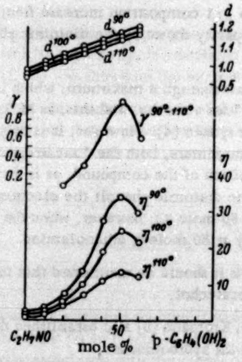

Fig. 6. Ethanolamine-hydroquinone system: density, viscosity and its temperature coefficient.

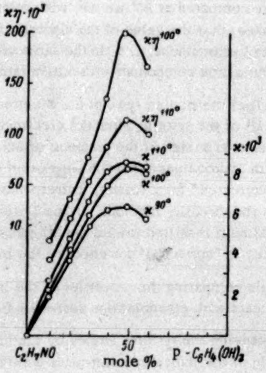

Fig. 7. Electroconductivity of the system ethanolamine-hydroquinone.

Ethanolamine-hydroquinone system. The fusion diagram of this system (Fig. 1, Curve c) shows two eutectics, corresponding to 75 and 40 mole % ethanolamine and having m.p. −5° and 67° respectively; and also one maximum, corresponding to ethanolamine-hydroquinone compound with a 1 : 1 composition, and melting at 77°. The viscosity and electroconductivity of the given system were measured at 90, 100 and 110°. The viscosity, density and electroconductivity isotherms were taken up to only 60 mole % hydroquinone, due to its crystallization.

In this system the curves of the viscosity (Fig. 6) and of its temperature coefficient show maxima, corresponding to 50 mole % of ethanolamine in the mixture. The density isotherms appear as curves that are concave to the composition axis, which indicates the contraction found in the system.

The electroconductivity isotherms (Fig. 7) appear as curves with a maximum, which is found at an equimolar ratio of the components.

The "corrected" electroconductivity isotherms appear as curves that fall exactly on 50 mole % ethanolamine.

As a result, the presence of maxima on the viscosity, temperature coefficient of the viscosity and "corrected" electroconductivity curves, found at an equimolar ratio of the components, indicates that the compound, shown by the fusion method to have a 1 : 1 compositon, is stable in the liquid phase.

Heating was observed in all three systems when the components were mixed.

DISCUSSION OF RESULTS

A study of the fusion of the binary systems formed by ethanolamine with the isomeric diatomic phenols revealed that all three isomers with ethanolamine form a compound with an equimolar composition. The presence of a flat maximum on the fusion diagrams of the given systems indicates that the compounds that are formed here show partial decomposition into their components when melted. In all three systems the viscosity isotherms pass through a maximum in the region of 50 mole % of the components; this indicates that the compounds, shown by the fusion method to have an equimolar composition, are stable in the liquid phase.

In comparing the viscosity isotherms of the systems formed by stannic chloride with esters, N. S. Kurnakov [3] concluded that the viscosity isotherms of the systems in which one of the components is a member of a homologous series permit making certain conclusions relative to the change in affinity found in these systems. It is evident that in some cases a comparison of the viscosity isotherms for systems in which one of the components appears as an isomer of the same compound, permits judging to a certain extent the influence shown by isomerization on the affinity magnitude. Consequently, when the viscosity isotherms of our studied binary systems are compared at 90° we see, with relatively close numerical values for the viscosities of the diatomic phenols taken, that the value of the viscosity for the compounds with a 1:1 composition increase from pyrocatechol to hydroquinone, i. e. in the same order as the increase in capacity shown by the diatomic phenols to form crystalline compounds with ethanolamine.

In all of the studied systems the electroconductivity isotherms pass through a maximum, which is retained in all of the systems when the electroconductivity is "corrected" for viscosity, and this, as M. I. Usanovich observes, is a sign of the presence of acid-base interaction in the system [4]. However, it is only in the system with hydroquinone that the position of the electroconductivity maximum, both the "uncorrected" and the one "corrected" for viscosity, corresponds to an equimolar composition of the compound, as is shown by the fusion and viscosity methods. In the systems with the other isomeric diatomic phenols the electroconductivity maximum is shifted toward the ethanolamine side (up to 70 and 80 mole %); however, when the electroconductivity is "corrected" for viscosity the maximum is found exactly at 50 mole % ethanolamine.

While comparing the properties of the indicated diatomic phenols it should be mentioned that the tendency to react with ethanolamine decreases from hydroquinone to pyrocatechol.

In studying the systems formed by diatomic phenols with aniline, Kremann [5] also established that the most stable of the indicated compounds was the compound of aniline with hydroquinone.

SUMMARY

1. The fusion, viscosity, density and electroconductivity of the binary systems formed by ethanolamine with pyrocatechol, resorcinol and hydroquinone were studied.

2. It was established that ethanolamine forms compounds of equimolar composition with all three isomers. Of the three isomeric diatomic phenols the greatest affinity toward ethanolamine is shown by hydroquinone.

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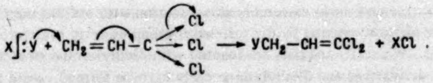
THE INFLUENCE OF NUCLEOPHILIC SUBSTANCES ON COMPOUND OF STRUCTURE $CCl_3CH=CRR'$

A. N. Nesmeyanov, R. Kh. Freidlina, L. I. Zakharkin and A. B. Belyavsky

The trichlormethyl group in saturated polychlorohydrocarbons is inert to the influence of nucleophilic reagents, which, apparently, is associated with the screening of the electrophilic carbon atom by the three chlorine atoms [1]. As was shown on the example of 1,1,1-trichloropropene [2], in compounds containing the $>C=\underset{|}{C}=CCl_3$ grouping the electrophilic nature of the carbon atom in the trichloromethyl group is transmitted along the chain by σ,π-conjugation to the γ-carbon atom, as a result of which the reaction of 1,1,1-trichloropropene with nucleophilic reagents proceeds with transfer of the reaction center in accord with Scheme 1:



$$X\rfloor\!:Y + CH_2=CH-C\begin{smallmatrix}Cl\\Cl\\Cl\end{smallmatrix} \longrightarrow YCH_2-CH=CCl_2 + XCl\,. \qquad (1)$$

In accord with this scheme it can be expected that the reaction capacity shown by compounds of structure $CCl_3-CH=CCR'$ (I) in reactions of this type will depend to a strong degree on the nature of the substituents R and R', directly associated with the center of nucleophilic attack.

To study the influence of substituents on the reaction capacity shown by compounds of Type (I) we synthesized the substances with the structures:

$$\underset{(II)}{CCl_3-CH=CHCH_3},\ \underset{(III)}{CCl_3CH=CHC_6H_5},\ \underset{(IV)}{CCl_3CH=C(CH_3)_2},\ \underset{(V)}{CCl_3-CH=CH-C(CH_3)_3}.$$

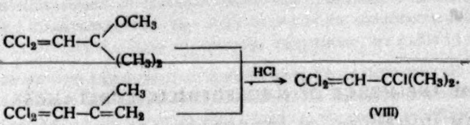
These compounds were synthesized by Scheme 2:

$$CCl_3Br + CH_2=CRR' \rightarrow \underset{(VI)}{CCl_3CH_2CBrRR'} \rightarrow \underset{(I)}{CCl_3-CH=CRR'}. \qquad (2)$$

To obtain (II) and (IV) we dehydrobrominated (VI) by its treatment with alcoholic potassium hydroxide solution under cooling. To synthesize (III) and (V) we used triethylamine as the dehydrobromination agent in the first case, and diethylamine in the second. The structure of (III) was shown by its hydrolysis (by heating with 90% acetic acid) to cinnamic acid, and the structure of (IV) by its alkaline hydrolysis to yield β,β-dimethylacrylic acid. The compounds having the Structures (VII) and (VIII) were synthesized being isomeric with (II) and (IV). Substance (VII) was obtained by Scheme 3:

$$CCl_2=CHCHO \xrightarrow{CH_3MgI} \underset{(IX)}{CCl_2=CHCHOHCH_3} \xrightarrow{HCl} \underset{(VII)}{CCl_2=CH-CHClCH_3}. \qquad (3)$$

As is known, the allylic rearrangement of compounds of Type (IX) fails to proceed in acid medium [11]. In accord with Scheme 4, Substance (VIII) was obtained by treating either 1,1,-dichloro-3-methoxy-3-methyl-1-butene or 1,1-dichloro-3-methyl-1,3-butadiene with hydrogen chloride:


(4)

The obtained isomers (II) and (VII), and also (IV) and (VIII), show extremely close physical properties—boiling point, refractive index and specific gravity, and for this reason a study of the isomerization of (II) into (VII) or of (IV) into (VIII) was not undertaken. We were unable to synthesize 1,1,3-trichloro-3-phenylpropene, since the treatment of 1,1-dichloro-3-hydroxy-3-phenyl-1-propene with thionyl chloride give 1,1,1-trichloro-3 phenyl-2-propene, due to the rearrangement that occurred here.

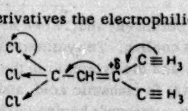
In the present work we studied the influence of nucleophilic reagents on compounds of type $CCl_3-CH=CRR'$. As nucleophilic substances we used ammonia and amines, alcohols in the presence of alkali and sodium alcoholates, sodium sulfide and sodium thiophenolate, potassium acetate and some other compounds.

In all of the studied cases the reactions proceeded with transfer of the reaction center in accord with Scheme 1. In this connection the following characteristics were observed: 1,1,1-trichloro-4,4-dimethyl-2-pentene fails to react with diethylamine and shows extremely slow reaction with sodium methylate, which apparently is associated with the steric hindrance, created by the tert-butyl group directly associated with the center of nucleophilic attack (see Scheme 1). When (II) and (III) are reacted with diethylamine in alcohol medium a mixture of the corresponding alkoxy derivatives and diethylamino derivatives is formed, while in the case of (IV) and (V) only the alkoxy derivative is formed. It had been shown earlier [2] that $CH_2=CH-CCl_3$ under similar conditions gives only the diethylamino derivative. When (II) and (III) were reacted with diethylamine in the absence of alcohol the reaction proceeded normally, giving the diethylamino derivatives, while (IV) fails to react even at 100-110°, with tarring being obtained at higher temperatures. The reaction of (IV) with either ammonia or piperidine in alcohol medium gave very small amounts of amino derivatives. A similar behavior was observed in the reactions with sodium sulfide in alcohol medium, where $CCl_3CH=CH_2$ gave only the sulfide of structure $(CCl_2=CH-CH_2)_2S$, and (IV) only the corresponding alkoxy derivative. The obtained data are summarized in the table.

As can be seen from the data given in the table, the studied substances can be arranged in the order:

$$CCl_3-CH=CH_2;\ CCl_3CH=CHCH_3;$$
$$CCl_3CH=CHC_6H_5;$$
$$CCl_3CH=CH-C(CH_3)_3\ CCl_3CH=C(CH_3)_2,$$

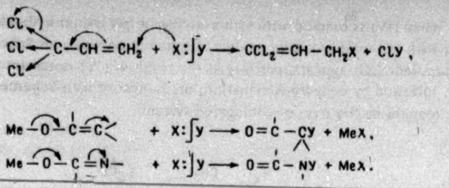
in which the capacity shown by the examined compounds for alkylation on the nitrogen decreases, and increases on the oxygen.

If it is assumed that in the above presented order of trichloromethyl derivatives the electrophilicity of the γ-carbon atom decreases, being least for the γ,γ-dimethyltrichloropropene , then the observed rule can be formulated as follows: with decrease in the electrophilic properties shown by compounds the rate of oxygen-alkylation increases and that of nitrogen-alkylation decreases.

In some respects the reactions based on Scheme 1 are just the opposite of the alkylation reactions shown by metallic derivatives of tautomeric systems (Schemes 5 and 6) proceeding with transfer of the reaction center:

Influence of Nucleophilic Reagents on $CCl_3CH=CRR'$

Nucleophilic reagent	Character of substitution in				
	$CCl_3CH=CH_2$*	$CCl_3CH=CHCH_3$	$CCl_3CH=CHC_6H_5$	$CCl_3CH=C(CH_3)_2$*	$CCl_3-CH=CH-C(CH_3)_3$
R_1ONa (in alcohol)	On O**	On O	On O	On O	On O
$(C_2H_5)_2NH$	On N***	On N	On N	Fails to substitute	Fails to substitute
$(C_2H_5)_2NH$ (in alcohol)	On N	On O and on N	On O and on N	On O	On O
Na_2S (in alcohol)	On S****	On O and on S		On O	–



(1)

(5)

(6)

The difference between Scheme 1, on the one hand, and Schemes 5 and 6, on the other, is that in the first case the transfer of the reaction center is accomplished in the molecule of the alkylating reagent, and in the latter, in the molecule of the alkylated compounds [4, 5].

At the present time there is much data to show that in the alkylation of compounds of the type of either $-N=\overset{|}{C}-OMe$ or $>C=\underset{|}{C}-O-Me$, in which the O–metal bond shows weak ionization, strongly electrophilic reagents function mainly as either nitrogen or (correspondingly) carbon-alkylation agents, and weakly electrophilic reagents as oxygen-alkylation agents. Thus, for example, the copper salt of acetoacetic ester is acylated by ethyl chlorocarbonate on the carbon, and by benzoyl chloride (less electrophilic) on the oxygen [6]. As a result, a similarity in the direction of reaction was observed when the alkylation of substances, in which the two centers of electrophilic attack are linked in the system by σ,π-conjugation (keto-enol, lactim-lactam) in one molecule, was compared with the alkylation of a mixture of two substances, containing the same centers of electrophilic attack. Further study of this phenomenon is of interest.

We will discuss some of the other reactions of the studied substances. Similar to 1,1,1-trichloropropene [7], the trichloromethyl derivatives (II), (III) and (IV) show condensation with benzene in the presence of aluminum chloride to give compounds with the structures:

$$C_6H_5CH(CH_3)-CH=CCl_2,\ (C_6H_5)_2CH-CH=CCl_2,$$
$$C_6H_5C(CH_3)_2CH=CCl_2.$$

The dehydrobromination of $CCl_3CH_2-CBr(CH_3)_2$ (X) with alcoholic caustic at 0° gives, together with (IV), also $CCl_2=CH-C(CH_3)=CH_2$(XI).

The treatment of (X), and also of $CCl_3-CH_2C(CH_3)_2Cl$, with excess alkali in either methyl or ethyl alcohol medium at room temperature leads to the corresponding alkoxy derivatives:

$$CCl_2=CHC(CH_3)_2OCH_3\ (XII)\ \text{and}\ CCl_2=CHC(CH_3)_2OC_2H_5\ (XIII).$$

The last compound when heated cleaves a molecule of alcohol and is converted into (XI). Treatment of either (XI) or (XII) with hydrogen chloride gives the compound of structure $CCl_2=CHC(CH_3)_2Cl$, easily cleaving hydrogen chloride to give (XI) when treated with alcoholic caustic.

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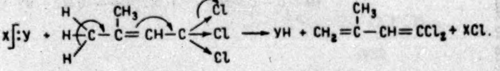
* Based on the data of [2].

** On O denotes obtaining $CCl_2=CH-CRR'(OR_1)$.

*** On N denotes obtaining $CCl_2=CH-CRR'(NR_2)$.

**** On S denotes obtaining $[CCl_2=CH-CRR']_2S$.

When (IV) is reacted with either alcoholic potassium hydroxide solution, diethylamine or piperidine, together with the main reaction product formed in accord with Scheme 1, a small amount of 1,1-dichloro-methyl-1,3-butadiene (XI) appears, possibly as the result of (IV) isomerizing into 1,1,3-trichloro-3-methyl-1-butene (VIII), followed by dehydrochlorination, or, in accord with Scheme 7, as the result of direct action of the nucleophilic reagent on the σ,π,σ-conjugated system:



(7)

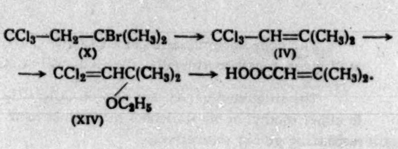
In support of the second postulation it can be mentioned that whereas the reaction of (IV) with alcoholic caustic yields mainly 1,1-dichloro-3-alkoxy-3-methyl-1-butene and only a small amount of 1,1-dichloro-3-methyl-1-3-butadiene (XI), (VIII) under the same conditions is completely transformed into (XI), which indicates that (IV) reacts with nucleophilic reagents by Scheme 1, and not through its preliminary isomerization into (VIII).

In some respects the chemical transformations shown by trichloromethyl group in (III) lie close to the transformations shown by the same group in benzotrichloride. Thus, (III) is easily hydrolyzed when it is heated for 30 minutes with 90% acetic acid to give cinnamic acid* in 95% yield, which shows disproportionation when heated with chloroacetic acid to give chloroacetyl chloride.

To prove the structure of the addition products of bromotrichloromethane to propylene, isobutylene and styrene, Kharasch and coworkers heated the indicated substances for a long time, first with sodium alcoholate, and then with aqueous caustic. From $CCl_3CH_2CHBrCH_3$ they obtained crotonic acid in a yield of ~8% of theory, Compound (X) showed smooth conversion into β,β-dimethylacrylic acid, and cinnamic acid was obtained from $CCl_3CH_2CHBrC_6H_5$, the yield of which was not indicated by the authors. They postulate that the reactions proceed in accord with Scheme 8:

$$RCHBrCH_2CCl_3 \rightarrow RCH{=}CHCCl_3 \rightarrow RCH{=}CHC(OC_2H_5)_3 \rightarrow RCH{=}CH{-}CO_2H. \qquad (8)$$

We found that when (IV) was reacted with alcohol, both in the presence of alkali (alcoholate) and in its absence, it is converted into the ethoxy derivative (XIV). The latter when boiled with sodium alcoholate, and then with aqueous caustic, gives dimethylacrylic acid. It is evident that the transformations based on Scheme 9 also proceeded under the experimental conditions used by Kharasch and coworkers:



$$\begin{gathered}\underset{(X)}{CCl_3{-}CH_2{-}CBr(CH_3)_2} \longrightarrow \underset{(IV)}{CCl_3{-}CH{=}C(CH_3)_2} \longrightarrow \\ \longrightarrow \underset{(XIV)}{CCl_2{=}CH\underset{OC_2H_5}{C}(CH_3)_2} \longrightarrow HOOCCH{=}C(CH_3)_2. \qquad (9)\end{gathered}$$

Evidently, the small yield of crotonic acid from (X) is asssociated with the fact that the intermediately formed ethoxy derivative $CCl_2{=}CH{-}\underset{OC_2H_5}{CH}CH_3$ is incapable of transformation into crotonic acid under these conditions.

EXPERIMENTAL

1. 1,1,1-Trichloro-2-butene. To a solution of 44 g of 1,1,1-trichloro-3-bromobutane in 50 ml of anhydrous alcohol was slowly added under cooling and stirring 11.2 g of potassium hydroxide in 50 ml of alcohol. Stirring

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[*] Kharasch and coworkers [8] described the hydrolysis of $CCl_3{-}CH_2CHBrC_6H_5$ to cinnamic acid by the use of a mixture of acetic and perchloric acids; we established that the reaction also proceeds without the addition of the perchloric acid.

of the mixture at 0° was continued for 6 hours, after which the reaction mass was diluted with water and extracted with ether. The ether extract was washed with water and dired over sodium sulfate. After distilling off the ether the residue was fractionated in vacuo. The yield of 1,1,1-trichloro-2-butene was 19.2 g (51%). After a second distillation the substance had b. p. 57-57.5° at 49 mm.

n_D^{20} 1.4810, d_4^{20} 1.2972, MR_D 34.71; calc. 34.80
Found %: C 30.41, 30.40; H 3.32, 3.28; Cl 66.26, 66.04. $C_4H_5Cl_3$. Calculated %: C 30.11; H 3.10; Cl 66.75.

A solution of 4.7 g of 1,1,1-trichloro-2-butene in chloroform was treated with 6% ozone for 4 hours. After the usual treatment the reaction mixture gave 2.8 g (50%) of chloral, which was identified as the hydrazone of structure $(NO_2)_2C_6H_3NH-N=CHCO_2C_2H_5$.

2. 1,1,3-Trichloro-1-butene. a) 1,1-dichloro-3-hydroxy-2-butene. An ether solution of 50 g of dichloroacrolein and an equivalent amount of methylmagnesium iodide was boiled for 2 hours. After the mixture was decomposed with a concentrated solution of ammonium chloride and worked up in the usual manner it gave 34 g (60%) of 1, 1-dichloro-3-hydroxy-1-butene with b.p. 72° at 10 mm.

n_D^{20} 1.4792, d_4^{20} 1.2745, MR_D 31.40; calc. 31.46.
Found %: Cl 50.02, 49.87. $C_4H_6OCl_2$. Calculated %: Cl 50.28

b) 1,1,3-Trichloro-1-butene. The heating of 18 g of 1,1-dichloro-3-hydroxy-1-butene with hydrochloric acid in the presence of zinc chloride gave 17.5 g (85%) of 1,1,1-trichloro-1-butene.

B.p. 68° at 52 mm, n_D^{20} 1.4815, d_4^{20} 1.3026, MR_D 34.92; calc. 34.82.

This compound adds bromine to yield dibromotrichlorobutane, boiling at 87° (1 mm).

n_D^{20} 1.5590, d_4^{20} 2.0466, MR_D 50.41; calc. 50.80.
Found %: C 15.42, 15.27; H 1.67, 1.49; (Br + Cl) 83.46, 83.78. $C_4H_5Cl_3Br_2$. Calculated %: C 15.10; H 1.52; (Br + Cl) 83.40.

The structure of the 1,1,1-trichloro-1-butene was shown by its ozonolysis to give phosgene, which was identified as diphenylurea with m.p. 232-233°. Its mixed melting point with known diphenylurea failed to be depressed.

3. 1,1,1-Trichloro-3-phenyl-2-propene. A mixture of 1,1,1-trichloro-3-bromo-3-phenylpropane and 275 g of triethylamine was boiled under heating in an oil bath for 8 hours. The excess triethylamine was removed by distillation under slight vacuum (190 g), and the residue was treated with dilute hydrochloric acid and extracted with ether. The ether solution gave 96 g (64%) of 1,1,1-trichloro-3-phenyl-2-propene.

B.p. 91 - 92° at 1 mm, n_D^{20} 1.5710, d_4^{20} 1.3217. (Literature [9]: B.p. 93-95° at 0.3 mm, n_D^{20} 1.5731).
Found %: C 48.49, 48.60; H 3.44, 3.34; Cl 47.82, 47.65. $C_9H_7Cl_3$. Calculated %: C 48.75; H 3.16; Cl 48.08

When alcoholic caustic is used for the dehydrobromination the 1,1,1-trichloro-3-phenylpropene that is formed shows secondary reaction with the alcohol.

A solution of 11 g of 1,1,1-trichloro-3-phenyl-2-propene in 30 ml of 90% acetic acid was heated for 90 minutes, and after dilution with water a yield of 7 g (95%) of cinnamic acid was obtained, m.p. 133° (from water).

4. 1,1,1-Trichloro-3-methyl-2-butene. A solution of 153 g of 1,1,1-trichloro-3-bromo-3-methylbutane in 50 ml of alcohol was treated at 0° with a solution of 45 g of potassium hydroxide in 180 g of alcohol. Fractionation of the reaction products through a column gave 3.5 g of 1,1-dichloro-3-methyl-1,3-butadiene (B.p. 30-31° at 8 mm, n_D^{20} 1.5027) and 63 g (60.5%) of 1,1,1-trichloro-3-methyl-2-butene.

B.p. 45-46° at 8 mm, n_D^{20} 1.4822, d_4^{20} 1.2497, MR_D 39.59; calc. 39.42.
Found %: C 34.63, 34.59; H 4.15, 4.01. $C_5H_7Cl_3$. Calculated %: C 34.58; H 4.03.

5. 1,1-Dichloro-3-methoxy-3-methyl-1-butene. The experiment was run in the same manner as the preceding, but at room temperature. From a mixture of 63 g of 1,1,1,3-tetrachloro-3-methylbutane and 47 g of potassium hydroxide in 150 ml of methyl alcohol, reacted at room temperature for a day, a mixture was isolated, which when fractionated through a column gave 5.1 g of 1,1-dichloro-3-methyl-1,3-butadiene and 36.2 g (71%) of 1,1-dichloro-3-methoxy-3-methyl-1-butene.

B.p. 51-52° at 10 mm, n_D^{20} 1.4628, d_4^{20} 1.1418, MR_D 40.78; calc. 40.89.
Found %: C 42.22, 42.23; H 6.19, 5.93. $C_6H_{10}OCl_2$. Calculated %: C 42.53; H 5.91.

1,1-Dichloro-3-methoxy-3-methyl-1-butene was obtained from 1,1,1-trichloro-3-bromo-3-methylbutane in a similar manner.

6. Alkaline hydrolysis of 1,1-dichloro-3-methoxy-3-methyl-1-butene. A solution of 17 g of 1,1-dichloro-3-methoxy-3-methyl-1-butene and sodium ethylate (from 6 g of sodium) in 80 ml of anhydrous ethanol was boiled for 10 hours, after which a solution of 8 g of potassium hydroxide in 10 ml of water was added, and the boiling was continued for another 6 hours. The alcohol was vacuum distilled, water was added to the residue, and the obtained solution was extracted with ether, made acid with hydrochloric acid. The acid solution was extracted with ether, and the ether extract was dried over calcium chloride. Removal of the ether gave β,β-dimethylacrylic acid. Yield 4.2 g, m.p. 69-70° (from water).

7. 1,1-Dichloro-3-ethoxy-3-methyl-1-butene. The treatment of 50 g of 1,1,1,3-tetrachloro-3-methylbutane with alcoholic potassium hydroxide (35 g KOH in 100 ml ethanol), similar to the preceding experiment, gave 12 g of 1,1-dichloro-3-methyl-1,3-butadiene and 14 g of 1,1-dichloro-3-ethoxy-3-methyl-1-butene.

B.p. 72-73° at 24 mm, n_D^{20} 1.4616, d_4^{20} 1.1101, MR_D 45.43; calc. 45.44.

When heated to its boiling point 1,1-dichloro-3-ethoxy-3-methyl-1-butene cleaves ethyl alcohol and is converted into 1,1-dichloro-3-methyl-1,3-butadiene.

8. 1,1,3-Trichloro-3-methyl-1-butene. a) A stream of dry hydrogen chloride was passed into 39.5 g of 1,1-dichloro-3-methoxy-3-methyl-1-butene for 2.5 hours. After some time two layers were formed. The reaction proceeded with noticeable self-heating. Then the mixture was poured into hydrochloric acid, the lower layer separated, washed twice with water, and dried over calcium chloride. Vacuum distillation gave 30.1 g of 1,1,3-trichloro-3-methyl-1-butene.

B.p. 58-58.5° at 15 mm, n_D^{20} 1.4847, d_4^{20} 1.2527, MR_D 39.58; calc. 39.42.
Found %: C 34.77, 34.84; H 3.98, 3.92. $C_5H_7Cl_3$. Calculated %: C 34.58; H 4.03.

b) A stream of dry hydrogen chloride was passed into a mixture of 14 g of 1,1-dichloro-3-methyl-1,3-butadiene and 1 g of zinc chloride at −5 to −7° for 3 hours. The reaction mixture was worked up the same as described above. Vacuum distillation gave 9.1 g (52%) of 1,1,3-trichloro-3-methyl-1-butene, b.p. 64° at 25 mm, n_D^{20} 1.4847. When treated with alcoholic caustic the substance is almost completely converted into 1,1-dichloro-3-methyl-1,3-butadiene and when stored it evolves hydrogen chloride.

9. 1,1,1-Trichloro-4, 4-dimethyl-2-pentene. a) 1,1,1-trichloro-3-bromo-4,4-dimethylpentane. The reaction between the bromotrichloromethane and 4,4-dimethyl-1-butene was run in a rotating autoclave made of stainless steel. The heating of 26 g of the olefin, 60 g of the bromotrichloromethane and 1 g of the dinitrile of azobisisobutyric acid at 100-105° for 6 hours gave 38 g of 1,1,1-trichloro-3-bromo-4,4-dimethylpentane.

B.p. 90° at 5 mm, n_D^{20} 1.5030, d_4^{20} 1.4792, MR_D 54.14; calc. 54.47.
Found %: C 29.82, 30.02; H 4.19, 4.35; (Cl + Br) 65.24, 65.97. $C_7H_{12}Cl_3Br$. Calculated %: C 29.76; H 4.29; (Cl + Br) 65.87.

b) 1,1,1-Trichloro-4,4-dimethyl-2-pentene. A mixture of 33 g (0.11 mole) of 1,1,1-trichloro-3-bromo-4,4-dimethylpentane and 23 g (0.33 mole) of diethylamine was heated on the boiling water bath for 18 hours. After treatment with water the organic layer was separated, washed with hydrochloric acid, then with water, and dried over sodium sulfate. The yield of 1,1,1-trichloro-4,4-dimethyl-2-pentene ws 16 g (70%).

B.p. 64-65° at 10 mm, n_D^{20} 1.4725, d_4^{20} 1.1403, MR_D 49.54; calc. 48.66.
Found %: C 41.37, 41.43; H 5.48, 5.42; Cl 52.15, 52.49. $C_7H_{11}Cl_3$. Calculated %: C 41.69; H 5.50; Cl 52.72.

Negative results were obtained when we attempted to dehydrobrominate the substance by treatment with alcoholic potassium hydroxide solution. Ozonization gave chloral, which was identified as described in Expt. 1.

10. Reaction of 1,1,1-trichloro-2-butene. a) With sodium methylate. A mixture of 35.6 g of the trichlorobutene and sodium methylate solution (from 4.98 g sodium in 50 ml methanol) was heated on the water bath for 2.5 hours. The resulting precipitate of sodium chloride was filtered, the filtrate diluted with water, and the organic layer separated and dried over sodium sulfate. Fractionation through a column gave 20.7 g (50%) of 1,1-dichloro-3-methoxy-1-butene.

B.p. 64° at 57 mm, n_D^{20} 1.4580, d_D^{20} 1.1722, MR_D 36.02; calc. 36.19.
Found %: C 38.22, 38.37; H 4.96, 5.07. $C_5H_8OCl_2$. Calculated %: C 38.70; H 5.16.

b) With diethylamine. A mixture of 15.9 g of 1,1,1-trichloro-2-butene and 18.3 g of diethylamine was boiled for 8 hours. The reaction mixture was diluted with water. The organic layer was separated and treated with hydrochloric acid, and the neutral products were separated. In its properties the substance of the neutral fraction (2.7 g) represents unreacted starting compound (b.p. 69-71° at 58 mm, n_D^{20} 1.4805). The hydrochloric acid solution was treated with 20% aqueous sodium hydroxide solution. The base that separated here was dried over sodium sulfate. Fractional distillation gave 10.4 g (50%) of 3-diethylamino-1,1-dichloro-1-butene.

B.p. 79.5-80° at 14 mm, n_D^{20} 1.4690, d_4^{20} 1.0470, MR_D 52.15; calc. 52.35.
Found %: C 48.87, 48.97; H 7.57, 7.46. $C_8H_{15}NCl_2$. Calculated %: C 49.00; H 7.70.
Hydrochloride has m.p. 167.5°.
Found %: N 5.99, 5.98. $C_8H_{16}NCl_3$. Calculated %: N 6.02.

The structure of the 3-diethylamino-1,1-dichloro-1-butene was shown by determining the mixed melting point of its hydrochloride with the hydrochloride obtained by the scheme:

$$CCl_2{=}CHCHO \xrightarrow{CH_3MgI} CCl_2{=}CH{-}CHOHCH_3 \longrightarrow CCl_2{=}CH{-}CHClCH_3 \longrightarrow$$
$$\longrightarrow CCl_2{=}CH{-}CHN(C_2H_5)_2(CH_3) \longrightarrow CCl_2{=}CH{-}CHN(C_2H_5)_2(CH_3)\cdot HCl$$

(see Expts. 2, 11)

c) With diethylamine in methyl alcohol medium. The experiment was run the same as described above, but in methyl alcohol medium (40 ml). Here the 3-diethylamino-1,1-dichloro-1-butene was obtained in 30% yield. 3-Methoxy-1,1-dichloro-1-butene was isolated from the neutral fraction.

B.p. 40-41° at 15 mm, n_D^{20} 1.4580, d_4^{20} 1.1851, MR_D 35.69; calc. 36.19.

d) With sodium acetate. A mixture of 32 g of 1,1,1-trichloro-2-butene, 32.8 g of sodium acetate, 50 g of glacial acetic acid and 0.5 g of potassium iodide was heated on the water bath for 18 hours. From the reaction mixture was isolated 21.2 g (59%) of substance, boiling at 83-84° (26 mm).

n_D^{20} 1.4590, d_4^{20} 1.2234, MR_D 40.91; calc. 40.83.
Found %: C 39.08, 38.89; H 4.35, 4.37; Cl 38.81, 38.98. $C_6H_8O_2Cl_2$. Calculated %: C 39.34; H 4.80; Cl 38.79.

That the obtained compound is 3-acetoxy-1,1-dichloro-1-butene was shown by its alcoholysis to yield 3-hydroxy-1,1-dichloro-2-butene.

B.p. 63° at 6 mm, n_D^{20} 1.4790, d_4^{20} 1.2735, MR_D 31.26. $C_4H_6OCl_2$. Calc. 31.46.

In all of its properties this alcohol is identical with the substance obtained by the action of methylmagnesium iodide on dichloroacrolein (see Expt. 2).

e) With sodium sulfide. A mixture of 30 g of 1,1,1-trichloro-2-butene, 29 g of $Na_2S \cdot 9H_2O$, 80 ml of alcohol and 10 ml of water was heated on the water bath for 6 hours. After removing the alcohol by distillation the residue was washed well with water and dried over sodium sulfate. Vacuum fractionation gave 10.6 g (40%) of bis-(1,1-dichloro-3-methyl-1-propenyl) sulfide.

B.p. 104° at 5 mm, n_D^{20} 1.5345, d_4^{20} 1.3156, MR_D 66.17; calc. 65.68.
Found %: C 34.15, 34.23; H 3.57, 3.51; Cl 51.05, 51.23. $C_8H_{10}Cl_4S$. Calculated %: C 34.32; H 3.60; Cl 50.64.

Together with the sulfide a low-boiling fraction was obtained, containing 3-ethoxy-1,1-dichloro-1-butene, which we were unable to isolate in the pure state.

f) With sodio-malonic ester. To sodio-malonic ester, prepared from 4.6 g of sodium and 32 g of malonic ester, in 80 ml of anhydrous alcohol, was added 24.4 g of 1,1,1-trichloro-2-butene. The mixture was boiled for 3 hours. From the reaction mixture was isolated 31.5 g (70%) of the ethyl ester of 5,5-dichloro-3-methyl-2-carbethoxy-4-pentenoic acid.

B.p. 107° at 1 mm, n_D^{20} 1.4605, d_4^{20} 1.1829, MR_D 65.57; calc. 65.57.
Found %: C 46.98, 46.97; H 5.96, 5.83. $C_{11}H_{16}O_4Cl_2$. Calculated %: C 46.66; H 5.65.

Hydrolysis of 20.7 g of the obtained substance (by boiling in a mixture of hydrochloric and acetic acids), followed by decarboxylation, gave 11.5 g (85.7%) of 5,5-dichloro-3-methyl-4-pentenoic acid.

B.p. 102° at 1 mm, n_D^{20} 1.4800, d_4^{20} 1.2739, MR_D 40.71; calc. 40.81.
Found %: C 39.39, 39.67; H 4.38, 4.44. $C_6H_8O_2Cl_2$. Calculated %: C 39.35; H 4.37.

g) With benzene in the presence of $AlCl_3$. To a solution of 10 g of 1,1,1-trichloro-2-butene in 25 ml of benzene under stirring was added 1.2 g of aluminum chloride. The mixture showed both self-heating and hydrogen chloride evolution. After stirring for 30 minutes some water was added, and the benzene layer was separated, washed with water and dried over calcium chloride. Vacuum distillation gave 8.9 g (70%) of 1,1-dichloro-3-phenyl-1-butene.

B.p. 73-74° at 1.5 mm, n_D^{20} 1.5423, d_4^{20} 1.1702, MR_D 54.08; calc. 54.05.
Found %: C 60.08, 59.94; H 5.10, 5.11. $C_{10}H_{10}Cl_2$. Calculated %: C 59.75; H 4.97.

The substance readily adds chlorine to yield 1,1,1,2-tetrachloro-3-phenylbutane.

B.p. 107-108° at 1.5 mm, n_D^{20} 1.5568, d_4^{20} 1.3634, MR_D 64.20; calc. 64.25.
Found %: C 44.32, 44.23; H 3.71, 3.85. $C_{10}H_{10}Cl_4$. Calculated %: C 44.12; H 3.68.

11. Reaction of 1,1,3-trichloro-1-butene with diethylamine. The heating of 36 g of 1,1,3-trichloro-1-butene with 36.5 g of diethylamine for 16 hours on the water bath, after the usual workup of the reaction mixture, gave 20.6 g of unreacted 1,1,3-trichloro-1-butene (b.p. 69-70° at 60 mm, n_D^{20} 1.4820) and 13.8 g of 3-diethylamino-1,1-dichloro-1-butene (b.p. 84-87° at 21 mm, n_D^{20} 1.4690, d_4^{20} 1.0472).

After two recrystallizations the hydrochloride of this base had m.p. 167.5° and failed to depress the melting point when mixed with the hydrochloride that was obtained by reacting diethylamine with 1,1,1-trichloro-2-butene (see Expt. 10b).

12. Reaction of 1,1,1-trichloro-3-phenyl-2-propene. a) With alcoholic potassium hydroxide. A solution of 15 g of 1,1,1-trichloro-3-phenyl-2-propene and 5.5 g of potassium hydroxide in 25 ml of anhydrous ethanol was allowed to stand at room temperature for 16 hours. Here 13.6 g (87%) of 1,1-dichloro-3-ethoxy-3-phenyl-1-propene was isolated in the usual manner.

B.p. 90-91° at 1 mm, n_D^{20} 1.5308, d_4^{20} 1.1822. (Literature [10]: b.p. 90-91° at 1 mm, n_D^{20} 1.5306, d_4^{20} 1.1820).

b) With diethylamine. A solution of 11 g of 1,1,1-trichloro-3-phenyl-2-propene and 12 g of diethylamine in 25 ml of anhydrous ethanol was heated for 8 hours. The usual treatment gave 4.5 g of 1,1-dichloro-3-ethoxy-3-phenyl-1-propene (b.p. 90-91° at 1 mm, n_D^{20} 1.5307) and 4.8 of 1,1-dichloro-3-diethylamino-3-phenyl-1-propene.

B.p. 98-99° at 1 mm, n_D^{20} 1.5335, d_4^{20} 1.1116, MR_D 72.09; calc. 71.84.

The hydrochloride of 1,1-dichloro-3-diethylamino-3-phenyl-1-propene had m.p. 149-150° (from alcohol + petroleum ether).

Found %: N 4.95, 4.87. $C_{13}H_{18}NCl_3$. Calculated %: N 4.75.

c) With benzene in the presence of aluminum trichloride. From 11 g of 1,1,1-trichloro-3-phenyl-2-propene in 20 ml of benzene and 3 g of aluminum chloride there was obtained 9.8 g (76%) of 1,1-dichloro-3,3-diphenyl-1-propene.

B.p. 142-143° at 1 mm, n_D^{20} 1.5951, d_4^{20} 1.2180, MR_D 73.38; calc. 73.53.
Found %: C 68.02, 68.15; H 4.69, 4.45. $C_{15}H_{12}Cl_2$. Calculated %: C 68.43; H 4.56.

13. Reaction of thionyl chloride with 1,1-dichloro-3-hydroxy-3-phenyl-1-propene. A mixture of 13 g of 1,1-dichloro-3-hydroxy-3-phenyl-1-propene and 26 g of thionyl chloride was allowed to stand at room temperature for 2 hours, and then heated at 50-60° for 1 hour. After removing the excess thionyl chloride by distillation the residue was vacuum distilled to give 13.2 g of 1,1,1-trichloro-3-phenyl-2-propene, b.p. 94-95° at 2 mm, n_D^{20} 1.5710, d_4^{20} 1.3231. Cinnamic acid is obtained in nearly quantitative yield when this substance is heated with 90% acetic acid.

14. Reaction of 1,1,1-trichloro-3-methyl-2-butene. a) with alcoholic potassium hydroxide. A solution of 17 g of the trichloride and 8.5 g of potassium hydroxide in 40 ml of methyl alcohol was allowed to stand at room temperature for 16 hours. The usual treatment gave a small amount of 1,1-dichloro-3-methyl-1,3-butadiene and 13.6 g (82%) of 1,1-dichloro-3-methoxy-3-methyl-1-butene, b.p. 47-48° at 7 mm, n_D^{20} 1.4630.

b) With diethylamine. A solution of 10 g of the trichloride and 16 g of diethylamine in 30 ml of methyl alcohol was heated for 10 hours. The reaction mixture was cooled and then poured into dilute hydrochloric acid. The neutral products were extracted with ether. The ether extract was washed with water and dried over calcium chloride. Vacuum distillation gave a small amount of 1,1-dichloro-3-methyl-1,3-butdiene and 7.5 g (77%) of 1,1-dichloro-3-methoxy-3-methylbutene, b.p. 57-58° at 14 mm, n_D^{20} 1.4641, d_4^{20} 1.1431. Alkalization of the hydrochloric acid solution failed to give the reaction product of diethylamine with 1,1,1-trichloro-3-methylbutene.

The boiling of a mixture of 10 g of 1,1,1-trichloro-3-methyl-2-butene and 20 g of diethylamine for 5 hours, and then its heating in an ampul at 110° for 8 hours, failed to give a reaction product. Eight grams of the starting chloride was recovered. A tar is formed when the mixture is heated at 170-180° for 6 hours.

c) With ammonia. A solution of 10 g of 1,1,1-trichloro-3-methyl-2-butene and 5 g of ammonia in 40 ml of anhydrous ethanol was heated in an ampul at 90-95° for 4 hours. The usual treatment gave 6 g of 1,1-dichloro-3-ethoxymethyl-butane (b.p. 72-73° at 21 mm, n_D^{20} 1.461) and 0.9 g of 1,1-dichloro-3-amino-3-methyl-1-butene.

B.p. 64-65° at 12 mm, n_D^{20} 1.4785, d_4^{20} 1.1488, MR_D 37.98; calc. 37.98. Hydrochloride has m.p. 180-181° (from alcohol + ether).

Found %: N 7.72, 7.63. $C_5H_{10}NCl_3$. Calculated %: N 7.35.

d) With piperidine. A solution of 8.7 g of 1,1,1-trichloro-3-methyl-2-butene and 16 g of piperidine in 40 ml of anhydrous alcohol was heated for 4 hours. The usual treatment gave a small amount of 1,1-dichloro-3-methyl-1,3-butadiene, 5 g of 1,1-dichloro-3-ethoxy-3-methyl-1-butene (b.p. 61-62° at 16 mm, n_D^{20} 1.4608) and 0.6 g of 1,1-dichloro-3-piperidino-3-methyl-1-butene, which without distillation was converted into the hydrochloride with m.p. 248-249° (from alcohol).

Found %: N 5.31, 5.33. $C_{10}H_{18}NCl_3$. Calculated %: N 5.41.

e) With thiophenol. A solution of 8.7 g of 1,1,1-trichloro-3-methyl-2-butene and sodium thiophenolate (from 8 g of C_6H_5SH) in 30 ml of anhydrous alcohol was heated for 4 hours. From the reaction mixture was obtained 6 g of 1,1-dichloro-3-ethoxy-3-methyl-1-butene and 2.1 g of 1,1-dichloro-3-methyl-1-butenyl phenyl sulfide.

B.p. 102-103° at 1.5 mm, n_D^{20} 1.5705, d_4^{20} 1.1988, MR_D 67.65; calc. 67.86.

Found %: C 53.61, 53.64; H 4.93, 4.98. $C_{11}H_{12}Cl_2S$. Calculated %: C 53.44; H 4.86.

The reaction of 1,1,1-trichloro-3-methyl-2-butene with sodium sulfide in methyl alcohol solution failed to give the corresponding sulfide, and instead only 1,1-dichloro-3-methoxy-3-methyl-1-butene was formed.

f) With benzene in the presence of aluminum chloride. The reaction of 16 g of 1,1,1-trichloro-3-methyl-2-butene in 60 ml of benzene with 1.5 g of aluminum chloride gave 11 g of 1,1-dichloro-3-methyl-3-phenyl-1-butene.

B.p. 80-81° at 1 mm, n_D^{20} 1.5411, d_4^{20} 1.1540, MR_D 58.55; calc. 58.66.

Found %: C 61.51, 61.54; H 5.62, 5.70. $C_{11}H_{12}Cl_2$. Calculated %: C 61.39; H 5.58.

The oxidation of 8.4 g of 1,1-dichloro-3-methyl-3-phenyl-1-butene with a solution of 12.5 g of potassium permanganate and 6.2 g of potassium hydroxide in 280 ml of water was run at 90° for 10 hours. After removing the manganese dioxide, acidification of the alkaline solution gave 4.9 g of $\alpha\alpha$-dimethylphenylacetic acid with m.p. 76-77° (from petroleum ether). (Literature [3]: m.p. 77-78°).

g) Behavior to heating. The heating of 10 g of 1,1,1-trichloro-3-methyl-2-butene in a solution of 10 g of glacial acetic acid at 100° resulted in the copious evolution of hydrogen chloride. After boiling for 1 hour the solution was cooled, poured into water, and extracted with chloroform. The chloroform extract was washed with soda solution and dried over calcium chloride. Vacuum distillation gave 7.1 g (90%) of 1,1-dichloro-3-methyl-1,3-butadiene.

B.p. 42-42.5° at 25 mm, n_D^{20} 1.5027, d_4^{20} 1.1537.

Found %: C 43.98, 43.06; H 4.58, 4.52. $C_5H_6Cl_2$. Calculated %: C 43.80; H 4.38.

When heated to its boiling point 1,1,1-trichloro-3-methyl-2-butene also cleaves hydrogen chloride and is converted into 1,1-dichloro-3-methyl-1,3-butadiene, the latter showing rapid polymerization in the air to yield a transparent resin.

h) Action of ethyl alcohol. The standing of a solution of 10 g of 1,1,1-trichloro-3-methyl-2-butene in 40 ml of anhydrous ethanol at room temperature for several days resulted in the evolution of 2.14 g of hydrogen chloride (theoret. 2.13 g). Distillation of the reaction products gave 7 g of 1,1-dichloro-3-ethoxy-3-methyl-1-butene, n_D^{20} 1.4620, apparently containing a small amount of the trichloro-3-methylbutene as impurity.

15. Reaction of 1,1,1-trichloro-4,4-dimethyl-2-pentene. a) with sodium methylate. 10 g 1,1,1-trichloro-4,4-dimethyl-2-pentene was heated on the water bath with sodium methylate solution (from 1.15 g of sodium in 50 ml of methanol) for 30 hours. From the reaction mixture was obtained 5 g (50%) of 1,1-dichloro-3-methoxy-4,4-dimethyl-1-pentene.

B.p. 60-61° at 9 mm, n_D^{20} 1.4620, d_4^{20} 1.0755, MR_D 50.35; calc. 50.05.

Found %: C 48.67, 48.79; H 7.07, 7.10; Cl 36.12, 36.19. $C_8H_{14}OCl_2$. Calculated %: C 48.73; H 7.01; Cl 36.04.

b) With diethylamine in methyl alcohol medium. A mixture of 7 g of the trichloride and 5 g of diethylamine in 15 g of methyl alcohol was heated on the water bath for 19 hours. Treatment of the reaction mixture in the usual manner gave 2.2 g of substance, in its properties identical with the above-described 1,1-dichloro-3-methoxy-4,4-dimethyl-1-pentene (n_D^{20} 1.4620, d_4^{20} 1.0800). Chlorine-containing products with basic properties were not found.

SUMMARY

1. The compounds with the following structures were obtained

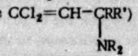
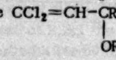
$$CCl_3{-}CH{=}CHCH_3,\ CCl_3CH{=}C(CH_3)_2,\ CCl_3CH{=}CHC_6H_5,$$
$$CCl_3CH{=}CHC(CH_3)_3,\ CCl_2{=}CH{-}CHClCH_3,\ CCl_2{=}CH{-}CCl(CH_3)_2$$

and their behavior toward nucleophilic reagents was studied.

2. It was found that compounds of structure $CCl_3CH{=}CRR'$, where RR' = H, CH_3; H, C_6H_5; CH_3, CH_3; H, and $C(CH_3)_3$, react with nucleophilic reagents under transfer of the reaction center to give compounds of structure $CCl_2{=}CH{-}CXRR'$, where X = OR, NR_2, SR, etc.

3. It was found for the series of compounds

$$CCl_3{-}CH{=}CH_2,\ CCl_3CH{=}CHCH_3,\ CCl_3CH{=}CHC_6H_5,$$
$$CCl_3{-}CH{=}CH{-}C(CH_3)_3,\ CCl_3CH{=}C(CH_3)_2,$$

capable of alkylating nucleophilic substances, that the ability to alkylate on the nitrogen (with the formation of compounds of the type  $CCl_2{=}CH{-}\underset{NR_2}{\underset{|}{C}}RR'$) decreases and the ability to alkylate on the oxygen (with the formation of compounds of the type  $CCl_2{=}CH{-}\underset{OR_1}{\underset{|}{C}}RR'$) increases.

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THE ROLE OF OXYGEN IN THE INITIAL STAGE OF VINYL CHLORIDE POLYMERIZATION

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Depending on their chemical nature and the conditions of running the process, molecular oxygen shows a dissimilar influcence on the polymerization of different monomers; consequently, it is not always possible to generalize the phenomena that appear for one or two monomers.

We deemed it necessary to elucidate the influence shown by oxygen on vinyl chloride when the monomer was subjected to polymerization in the absence of a catalyst, and also when different initiators were added, paying special attention to initiation of the polymerization reaction in the presence of air, since very little information has been published on this matter. It is only known that the polymerization of vinyl chloride under the influence of benzoyl peroxide, either in the mass or as an emulsion, proceeds more rapidly in a nitrogen atmosphere than it does in the air [1], and when heated in the absence of both oxygen and initiator the monomer fails to polymerize [2]. In addition, it seemed of interest to establish the interrelationship existing between the polymerization and oxidation processes. This problem also has failed as yet to receive its final solution [3].

A convenient method for studying the influence of oxygen on the polymerization process proved to be the iodometric determination of the perioxides that are always formed when the process is run in the presence of air.

Study of the initial period of noninitiated polymerization in the presence of air. In the block polymerization of vinyl chloride (in 70 ml ampuls) in the presence of air without the introduction of a foreign initiator an increase in the amount of peroxides was observed up to the point where traces of polymer appeared in the reaction system. The induction period depended on the amount of gas phase over the monomer. Thus, in ampuls with a ratio of gas phase to liquid of 8.3:1 the polymer failed to deposit even after 88 hours at 50°, while at a ratio of 4.7:1 the polymer deposited after 60 hours, and its amount increased with time.

An attempt was made to isolate the peroxides formed. After distilling off the monomer the residue gave a viscous yellowish liquid, which vigorously liberated iodine from potassium iodide solution. When carefully heated to 50° this liquid foamed and evolved HCl; when heated rapidly close to an open flame it exploded. After 88 hours of polymerization there was found 0.00238 g of peroxides, calculated as peroxide oxygen, in 9.08 g of the monomer.

Study of the initial period of initiated polymerization in the presence of air. The experiments were run in the presence of 0.3 mole % benzoyl peroxide (I), dinitrile of azoisobutyric acid (II), acetylbenzoyl perioxide (III), 2,2-azo-bis-p-isobutylpropyl nitrile (IV), methylamine-bis-diazo-p-anisole (V) and methylamine-bis-diazobenzene (VI). The experimental results for the determination of the amounts of peroxides formed during the induction period are shown in Fig. 1. In all of the experiments the amount of peroxides increased at a constant rate up to the moment of polymer precipitation, after which their amount dropped sharply, as can be seen from the data in Table 1. At the same time a considerable consumption of oxygen from the gas phase was established. During experiment the oxygen content dropped from 15.2 to 0.4%. Evidently, the increase in the amount of peroxides was due to their formation from the monomer and the oxygen contained in the gas phase.

As in the case of noninitiated polymerization, the length of the induction period depended on the volume of the gas phase over the monomer, i.e. on the potential supply of oxygen. Thus, when the polymerization of vinyl chloride was initiated by (II) at a temperature of 50° and a gas phase to liquid ratio of 5.4:1 the polymer deposited after 2 hours, while with a 15:1 ratio the polymer deposited after 7 hours. When (I) was used for the

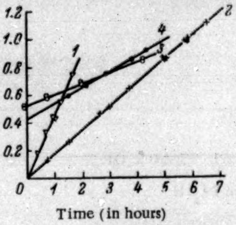

Fig. 1. Change in the concentration of peroxides at 50° as a function of the nature of the initiator (0.3 mole %).
1) 2,2-azo-bis-p-isobutylpropylnitrile, 2) dinitrile of azoisobutyric acid, 3) benzoyl peroxide, 4) acetylbenzoyl peroxide.

initiation there was found up to 350% of the original amount of peroxide at the end of the induction period, i.e. nearly twice as much as could have been formed from the decomposition of the initiator.

It is quite evident that such a large amount of peroxides could have been formed only as the reaction result of increase in chain length or as the reaction result of chain transfer. The chain transfer reaction is hardly possible in the investigated system. The peroxides that are found in the monomer are most probably polyperoxides, the existence of which was shown for methyl methacrylate and styrene [4].

It is interesting to mention that in comparing the polymerization activity of our investigated initiators, given in Table 2, with the rate of increase in the amount of peroxides a direct relationship between them is observed. Hardly any peroxides were obtained when initiators (V) and (VI) were used, although the decomposition rate of these compounds in a number of solvents is quite high. It should be mentioned that both (V) and (VI) initiate the polymerization of methyl methacrylate. The induction period for the initiated polymerization is considerably shorter than for the noninitiated, in which connection the more active the initiator the higher the rate for the formation of peroxides. This indicates the necessary participation of free radicals, formed in the decomposition of the initiator, in the given process. If it is assumed that the initiator is consumed at a rate equal to its natural decomposition, then it is evident that the kinetics for the formation of the peroxides is a function of the rate of initiator decomposition. Consequently, when polymerization is run in the presence of air it is possible to judge the reaction capacity shown by various initiators for a given monomer by the rate of increase in the amount of peroxides formed in the initial period.

TABLE 1

Change in the Amount of Peroxides with Appearance of Polymer in the Reaction Initiated by the Dinitrile of Azoisobutyric Acid at 50°

Reaction time (in hours)	Amount of 0.1N $Na_2S_2O_3$ consumed[*] (in ml)	External appearance
0	0	Clear solution
6.5	1.115	
9.0	0.497	Turbid solution
9.5	0.076	Polymer deposited
10.25	0.032	

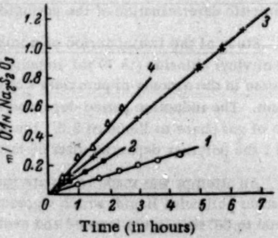

Fig. 2. Relation between rate of peroxide formation and initiator concentraction at 50°.
1) 0.1 wt %, 2) 0.35 %, 3) 0.5%, 4) 0.8%.

The experimental results, establishing the influence of initiator concentration on the rate of peroxide formation, for the case of initiation with (II), are shown in Fig. 2. As can be seen, an increase in the concentration of initiator in the monomer causes an increase in the rate at which the peroxides are formed that is proportional to the square root of the initiator concentration (Fig. 3).[**] This coincides with the relation existing between the polymerization rate and the initiator concentration and permits postulating the same mechanism for the process.

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[*] The data given in the tables and graphs for the consumption of 0.1N $Na_2S_2O_3$ are calculated on the basis of 1g of vinyl chloride.

[**] The value of K is proportional to the reaction rate constant and is expressed by the ratio of the amount of 0.1N $Na_2S_2O_3$ consumed to reaction time.

TABLE 2

Polymerization Activity of Various Initiators at 50° in Percents of Amount of Polymerized Monomer.*

Initiator	Time of polymerization (in hours)									
	4	6	8	10	12	14	16	18	20	24
Benzoyl peroxide	–	–	10	16	31.2	47.5	70	85.5	–	90.5
Azoisobutyric acid dinitrile	12	25	42	67	84	92	92	92	–	–
Acetylbenzoyl peroxide	11	–	26.5	42.5	65	81.5	95	–	–	–
2,2-Azo-bis-p-isobutylpropyl nitrile	29	72	90	90	–	–	–	–	–	–
Methylamine-bis-diazo-p-anisole	Fails to initiate									
Methylamine-bis-diazobenzene	Fails to initiate									

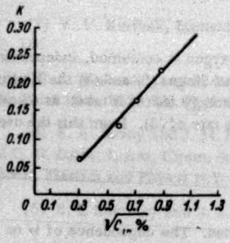

Fig. 3. Relation between the values of K and $\sqrt{C_{in.}}$.

The influence of temperature on the kinetics of forming peroxides under initiation with (II) is shown in Fig. 4. Graphically this relation has a linear character, in which connection the higher the reaction temperature the higher the rate of forming peroxides. From the plot of logarithm K vs. reciprocal of the temperature (Fig. 5) the energy of activation of the complete process E was calculated, which proved to be equal to 15.5 kcal./mole. From this it is easy to determine the energy of activation for the stage of initiator decomposition into free radicals in the monomer from the equation:

$$E = \frac{1}{2} E_{in} + E_{incr} - \frac{1}{2} E_{rev}$$

Taking $E_{\text{reversible}} \leq 2$ kcal./mole, we obtained that $E \leq 24$ kcal./mole. The activation energy for the decomposition into free radicals, calculated from the bond energies, proves to be ~35 kcal. The lack of agreement between these values leads to the conclusion that the adopted scheme [5] of initiation in two stages

$$RR \rightarrow 2R^{\cdot}, \tag{1}$$

$$R^{\cdot} + M \rightarrow RM^{\cdot} \tag{2}$$

fails to reflect the actual course of the process. In all probability, elementary Stages (1) and (2) are united into one. Evidently, here the facilitating influence of a solvent is manifested, which in our case is the monomer. Complexes should be formed when the initiator is dissolved in the monomer, the existence of which is determined by the polarity of the solute and solvent molecules. In this connection the more polar the molecules the more stable the complex, and the less probable the secondary decomposition of the initiator. The decomposition rate of the initiator sharply changes as a function of the nature of the solvent used. Here it is evident that the following circumstances should be valid: the more the solvent facilitates primary decomposition the less probable is secondary decomposition, and the more the activation energy of the initiation stage differs from that calculated from the bond energies.

The mechanism for the initial stage of vinyl chloride polymerization in the presence of air can be depicted as follows: at first active polymerization centers are formed as the result of the complex decomposing, after which the free radicals actively react with oxygen, giving compounds of the peroxide type.

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* The experiments were run by V. A. Lisovtsev and G. A. Stolyarenko under the supervision of L. V. Stupen.

$$RR + 2M \longrightarrow 2RM^{\cdot} \qquad (3)$$

$$RM^{\cdot} + O_2 \longrightarrow RMO_2^{\cdot} \ldots\ldots \longrightarrow \text{polyperoxides} \qquad (4)$$

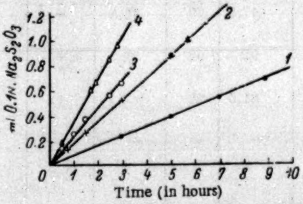

Fig. 4. Change in the rate of forming peroxides as a function of the reaction temperature at an initiator concentration of 0.3 mole%.
1) 40°, 2) 50°, 3) 55°, 4) 60°.

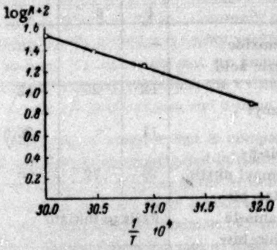

Fig. 5. Relation between the temperature and the rate of forming peroxides.

Stage (4), suppressing the polymerization reaction, proceeds until all of the oxygen is consumed, independent of whether or not a foreign initiator is present in the reaction mixture. Of the two Stages (3) and (4) the limiting one will be Stage (3), since it is extremely slow. Actually, if the activation energy for (4) is taken as 4 kcal., then the rate of (4) on Initiator (II) at 50° is approximately $10^7 - 10^8$ times the rate of (3). From this the overall polymerization rate is expressed thus:

$$W = K_{\text{in.}}^{1/2} K_{\text{equil.}} K_{\text{reversible}}^{-1/2} [C_{\text{in.}}]^{1/2} [M]^2$$

where $[C_{\text{in.}}]$ is the initiator concentration, and M is the monomer concentration. The dependence of W on $[C_{\text{in.}}]^{1/2}$ and on $[M]^2$ has been observed in a number of cases in mass polymerization [2].

Study of the initial period of noninitiated polymerization in the absence of air. The experimental results revealed that the thermal polymerization of vinyl chloride, run in the absence of both oxygen and foreign initiators, fails to take place, which is in full accord with the literature data [2]; in this connection peroxides were not revealed.

Study of the initial period of initiated polymerization in the absence of air. The experiments were run in presence of (I) and (II). The results of the experiments, run in the presence of (II), are summarized in Table 3. Analogous results were obtained for the case of initiation with (I).

TABLE 3

Duration of the Induction Period in Oxygen-free Polymerization, Initiated by the Dinitrile of Azoisobutyric Acid at 50°

Reaction time (in min.)	Consumption of 0.1N $Na_2S_2O_3$ (in ml)	External appearance
3	0.0165	Clear solution
6	0.0110	Turbid solution
9	0.0060	Polymer deposited
10	0.0165	
60	0.0110	

At the present time it can be considered established that for polymerization by the unbranched mechanism in homogeneous systems and with a low viscosity for the polymer solution the presence of an induction period greater than 1-3 minutes is always associated with the presence of inhibitors. In heterogeneous systems, and also in the presence of reaction branches, the duration of the induction period has still not been sufficiently elucidated. The data of the present study have shown that for either the mass or suspension polymerization of vinyl chloride the induction period also fails to exceed 3 minutes. The presence of a long induction period, observed in a number of cases, is determined by the presence of inhibitors, and in particular, by oxygen.

SUMMARY

1. The role of oxygen in the initial stage of vinyl chloride polymerization was studied. It was established that under the given conditions molecular oxygen functions as a polymerization inhibitor, independent of whether the polymerization is run in the presence or absence of a foreign initiator.

2. It was established that oxygen is consumed from the gas phase during the induction period. The duration of the induction period depends on the supply of oxygen in the system.

3. It was shown that the concentration of peroxides increases during the induction period when the polymerization of vinyl chloride is run in the presence of air. The point at which the solid polymer begins to form coincides with the conclusion of oxygen absorption.

4. The method of determining the increase in peroxide numbers during the initial period of vinyl chloride polymerization in the presence of air can be used to characterize the activity of initiators for a given monomer.

5. The oxidation and polymerization reactions appear as concurrent reactions. In the presence of oxygen in the system the oxidation reaction suppresses the polymerization reaction.

6. A mechanism was proposed for the initial stage of polymerizing vinyl chloride in mass.

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STUDY OF THE PROCESS FOR THE CATALYTIC HYDROPOLYMERIZATION OF ACETYLENE TO DIVINYL OVER PALLADIUM CATALYST

Yu. A. Gorin and N. L. Derevyagina

Of the reactions for the addition of various substances to acetylene great interest is shown by its hydrogenation reaction, which on nickel, palladium and other metallic catalysts is accompanied by the hydropolymerization process [1-3].

As A. D. Petrov and L. I. Antsus have shown, the catalytic hydropolymerization of acetylene, proceeding on nickel and mixtures of nickel with either $ZnCl_2$ or $CoCl_2$, depending on the conditions, leads to the formation of either normal butylenes or of isobutylene, or of their mixture. Divinyl was either absent in the reaction products or was found in small amounts [4]. It is known that the hydrogenation of acetylene and its derivatives on palladium proceeds selectively, in which connection the triple bond is changed to a double bond [5]. The reaction for the hydropolymerization of acetylene under the influence of palladium, with an adequate qualitative and quantitative characterization of the products that are formed, has not been studied.

The reaction mechanism for the hydropolymerization of acetylene still remains obscure. A. D. Petrov and coworkers have proposed a scheme of linear and nonlinear hydropolymerization of acetylene on a mixture of nickel with the chlorides of either zinc or cobalt [6,7]. However, the scheme of these authors fails to reflect the participation of hydrogen in the reaction of making the molecule more complicated. Sheridan, who studied the hydropolymerization of acetylene on a nickel-on-pumice catalyst [2], depicts this process as a chain reaction of the free radicals found on the catalyst surface. According to Vassiliev the first act in the process for the linear polymerization of acetylene on nickel [3] consists in the formation of a dimer by reaction of the acetylene molecules with the ethylene that is formed in the first stage of the hydrogenation. The further process of making more complicated molecules proceeds only via the coupling of ethylene with the corresponding olefins, and acetylene fails to participate here. In addition to the fact that such a representation fails to agree with the tendency shown by acetylene to polymerize, it also contradicts the data of Petrov and Sheridan [2], who established that ethylene, added to a mixture of hydrogen and acetylene in the presence of nickel behaves as an inert diluent.

The problem of the present investigation was to study the process for the hydrogenation and hydropolymerization of acetylene on a palladium catalyst for the purpose of determining the possibility and conditions of forming divinyl in one step and to elucidate the mechanism of this reaction.

We established that on a palladium catalyst (palladium on clay), together with hydrogenation of the acetylene to ethylene and ethane, and in part to methane, there proceeds hydropolymerization of the acetylene to yield a mixture of divinyl,* normal butylene and small amounts of isobutylene. As a result, the process for the hydropolymerization of acetylene is directed primarily toward the formation of linear hydrodimers. Together with gaseous hydrocarbons, we also observed the formation of liquid hydrocarbons. A study of a series of contact catalysts, containing various amounts of palladium (from 0.1 to 10%), revealed that the maximum yields of hydrodimers (divinyl and n-butylene) were attained at 335-340° (Table 1) on a catalyst containing not less than 1% of palladium (Fig. 1, Curve 3).

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* After we had completed the present study we learned from a brief note that the Japanese chemist Takesshima [8] obtained a small amount of divinyl from a mixture of acetylene and hydrogen on a palladium catalyst.

TABLE 1

Influence of Temperature on the Yield of Acetylene Hydrodimers

Expt. No.	Temperature	Degree of acetylene conversion (in %)	Yield of hydrodimers based on reacted acetylene (mole %)		
			C_4H_6	C_4H_8	$C_4H_6 + C_4H_8$
1	180°	27.8	–	–	13.2
2	180	28.3	–	–	14.2
3	185	28.0	–	–	13.8
4	335	55.7	11.6	8.2	19.8
5	340	55.4	11.4	7.6	19.0
6	335	58.0	10.0	8.3	18.3
7	460	14.0	–	–	7.4
8	450	28.6	–	–	9.7
9	440	20.0	–	–	11.8

A study of the conversion of acetylene alone revealed that in the absence of hydrogen the process for the polymerization of acetylene is practically nonexistent. The catalytic interaction of acetylene and hydrogen becomes noticeable only when there is about 12% hydrogen in the starting acetylene-hydrogen mixture (Fig. 2).

When the initial hydrogen concentration is increased from 12 to 50% the degree of acetylene and hydrogen conversion increases; the total yield of gaseous reaction products increases chiefly as the result of an increase in the amounts of ethylene and butylene. The yield of ethane remains constant; the yield of liquid products based on unreacted acetylene (tentatively calculated by the difference between the amount of reacted acetylene and the sum of all of the gaseous reaction products) decreases. The curves for the formation of ethylene (the hydrogenation product of acetylene) and for the sum of butylene plus divinyl (hydrodimerization products of acetylene) show the same character and pass through a maximum at the same initial hydrogen concentration (about 50%). As a result, the reaction for the dimerization of acetylene proceeds simultaneously with its hydrogenation reaction, and does not precede the latter. The break on both the hydrogenation and hydrodimerization curves corresponds to nearly complete exhaustion of the acetylene. Above the indicated initial hydrogen concentration the reaction for the complete hydrogenation of acetylene begins to predominate with the formation of ethane, and in part, of methane. The yields of the other products diminish in proportion to the increase in the initial hydrogen concentration.

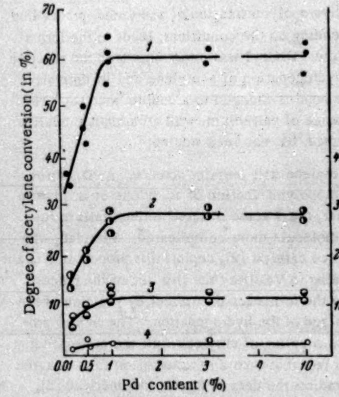

Fig. 1. Influence of the Pd content on the degree of acetylene conversion and yields of products (based on acetylene passed through).
1) C_2H_2, 2) C_2H_4, 3) $C_4H_6 + C_4H_8$, 4) $C_2H_6 + CH_4$.

At a relatively low hydrogen content in the starting mixture the main hydrodimerization product of acetylene is divinyl (Fig. 3). Increasing the initial hydrogen concentration results in decreasing the divinyl yield and increasing the butylene yield. As a result, the butylene that is formed in the acetylene hydropolymerization process is probably the hydrogenation product of divinyl. Apparently, divinyl fails to arise as the result of hydrogenating vinylacetylene, since we failed to obtain vinylacetylene when pure acetylene (without hydrogen) was passed over palladium catalyst. The maximum yield of divinyl, being about 6 mole % based on passed acetylene and about 11 mole % based on reacted acetylene, was obtained with the catalyst containing 1% palladium, at a temperature of 340-350°, and an initial hydrogen concentration of 30-35%. The data of the experiments run to elucidate the influence of the contact time (degree of acetylene conversion) on the yield of reaction products supported the postulation made above that butylene is formed as the result of divinyl hydrogenation. With a shorter contact time, and correspondingly a lower degree of acetylene conversion (Fig. 4), the divinyl yield increases, while the butylene yield approaches zero (Fig. 5).

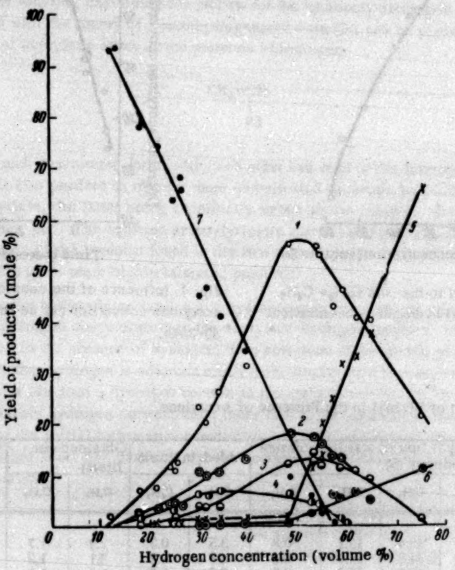

Fig. 2. Yield of products (based on passed acetylene) as a function of the initial hydrogen concentration.
1) C_2H_4, 2) $C_4H_6 + C_4H_8$, 3) C_4H_8, 4) C_4H_6, 5) C_2H_6, 6) CH_4, 7) % unreacted acetylene.

TABLE 2

Hydrogenation of Acetylene-Ethylene Mixtures*

Expt. No.	Composition of starting mixture (in volume %)			Composition of the starting mixture after substracting the ethylene (in volume %)		Degree of acetylene conversion (in %)	Yield of products based on reacted acetylene (in mole %)			
	C_2H_2	C_2H_4	H_2	C_2H_2	H_2		C_4H_6	C_4H_8	C_2H_4	C_2H_6+CH_4
1	32.8	32.7	34.5	48.6	51.4	96.7	4.0	14.0	57.5	12.6
2	32.2	35.0	32.8	49.5	50.5	94.8	6.0	13.8	55.0	7.4
3	66.2	–	33.8	66.2	33.8	58.7	11.5	6.7	45.3	4.5
4	46.8	–	53.2	46.8	53.2	95.0	4.5	13.9	58.0	14.5

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* For comparison the data of the experiments in which the starting mixture failed to contain ethylene (Expts. 3 and 4) are given in the table.

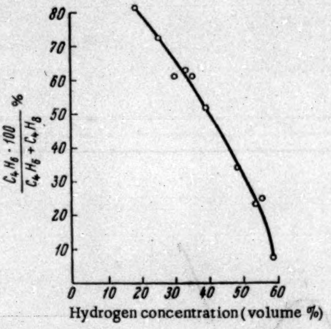


Fig. 3. Relation of divinyl to the sum $C_4H_6 + C_4H_8$ as a function of the initial hydrogen concentration.

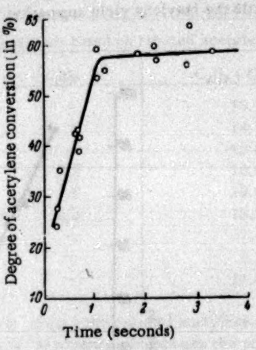


Fig. 4. Influence of the contact time on the degree of acetylene conversion (at an initial H_2 concentration of 30-33%).

TABLE 3

Hydrogenation of Divinyl in the Presence of Acetylene

Expt. Nos.	Composition of starting mixture (in volume %)				Added (in liters)		Obtained (in liters)		Conversion based on divinyl introduced into reaction (in %)
	H_2	C_2H_2	C_4H_6	C_4H_8	C_4H_6	C_4H_8	C_4H_6	C_4H_8	
1	40.6	45.4	13.2	0.8	3.5	0.2	2.9	1.7	17.0
2	40.0	44.8	14.4	0.8	3.8	0.2	3.1	1.8	18.5
3	39.7	49.6	10.2	0.5	2.2	0.2	1.9	1.3	13.6

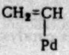
To study the mechanism of the acetylene hydropolymerization reaction we ran some experiments on the hydrogenation of ethylene and of divinyl, and we also studied the behavior of acetylene-ethylene-hydrogen and acetylene-divinyl-hydrogen mixtures. These experiments revealed that the hydrogenation of ethylene fails to be accompanied by the hydropolymerization process; only hydrogenation products are formed here: ethane and a small amount of methane. Ethylene, in admixture with hydrogen and acetylene, behaves like an inert diluent (Table 2, Expts. 1 and 2).

The hydrogenation of divinyl also fails to be accompanied by appreciable polymerization and leads to the formation of butylene. Here butane is obtained in very small amounts. When divinyl is hydrogenated in the presence of acetylene, then 14-18% of the divinyl introduced into reaction is converted into butylene and, possibly, other products (Table 3). If it is taken into consideration that part of the divinyl is formed under these conditions via acetylene hydrodimerization, then the true amount of divinyl that is converted into butylene will be considerably greater.

Study of the fraction of trimers with b.p. 79-81.5°, isolated by distilling the liquid hydrocarbons obtained in the acetylene hydropolymerization process, by the Raman spectra method revealed the presence of 2,4-hexadiene and small amounts of benzene. The presence of 2,4-hexadiene in this fraction was also shown by preparing the corresponding derivative with maleic anhydride.

The introduction of polymerization components into the composition of the palladium catalyst failed to increase the yield of divinyl. The investigated substances (phosphoric acid, synthetic aluminosilicate, copper phosphate and cobaltous chloride) failed to show any influence on the hydrogenation and hydropolymerization of acetylene.

At the base of the scheme, explaining the process for the hydropolymerization of acetylene on a palladium catalyst, in accord with the theory of a semihydrogenated state [9], can be placed the postulation that the semihydrogenated form of acetylene arises in the presence of hydrogen:



$$\mathrm{CH_2{=}}\underset{\mathrm{Pd}}{\mathrm{CH}} \qquad \mathrm{(I)}$$

The reaction of such unsaturated forms with each other can lead to the formation of a linear acetylene-divinyl hydrodimer. It is also possible to make a more complicated molecule by adding the semihydrogenated form to an acetylene particle, the latter being chemically sorbed on the catalyst, with the resultant creation of a semihydrogenated trimer, etc. The addition of catalytically active hydrogen to such semihydrogenated molecules leads to the formation of the products found in the first stage of saturation, namely ethylene and diolefins; their further hydrogenation gives more highly saturated products.

The processes for the hydropolymerization and hydrogenation of acetylene should be found in direct relationship to the initial hydrogen concentration in the acetylene-hydrogen mixture. Since the semihydrogenated form (I) cannot be formed in the absence of hydrogen, then acetylene alone cannot polymerize on a palladium catalyst. Due to the fact that hydrogen is adsorbed much more weakly than is acetylene [10], its concentration on the catalyst surface at a low initial hydrogen content in the acetylene-hydrogen mixture will be very small; consequently, below a certain hydrogen concentration there fails to be appreciable reaction between acetylene and hydrogen. Increasing the initial hydrogen concentration will faciliate the creation of a constantly greater amount of semihydrogenated acetylene particles and the development of both the acetylene hydrogenation and hydropolymerization reactions.

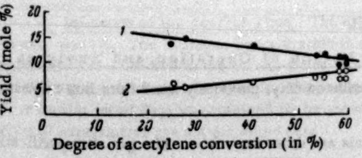
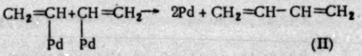


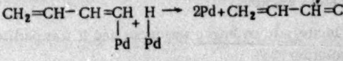
Fig. 5. Yields of divinyl and butylene (based on reacted acetylene) as a function of the degree of acetylene conversion (at an initial H_2 concentration of 30-33%).
1) C_4H_6, 2) C_4H_8.

In accord with the above the formation of divinyl can proceed either as the result of two semihydrogenated acetylene particles reacting with each other



$$\mathrm{CH_2{=}}\underset{\mathrm{Pd}}{\mathrm{CH}}\mathrm{+}\underset{\mathrm{Pd}}{\mathrm{CH}}\mathrm{{=}CH_2} \rightarrow \mathrm{2Pd + CH_2{=}CH{-}CH{=}CH_2} \qquad \mathrm{(II)}$$

or by the addition of a chemically sorbed acetylene molecule to the semihydrogenated form with subsequent hydrogenation of the resulting semihydrogenated acetylene dimer



$$\mathrm{CH_2{=}CH{-}CH{=}}\underset{\mathrm{Pd}}{\mathrm{CH}} + \underset{\mathrm{Pd}}{\mathrm{H}} \rightarrow \mathrm{2Pd{+}CH_2{=}CH{-}CH{=}CH_2} . \qquad \mathrm{(III)}$$

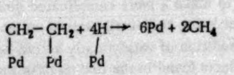
In its turn, the divinyl can be adsorbed on the catalyst and hydrogenated further to either 1-butene or 2-butene, depending on its orientation position on the catalyst surface (either the 1, 2 or 1, 4 atoms). In addition, the following isomerization is possible.

$$CH_2{=}CH{-}CH_2{-}CH_3 \rightleftharpoons CH_3{-}CH{=}CH{-}CH_3 \qquad (IV)$$

When the semihydrogenated form of the acetylene dimer reacts with the semihydrogenated acetylene particle the unstable, extremely unsaturated hexatriene should be formed, the hydrogenation of which leads to obtaining hexadiene. Since here the migration of double bonds should be expected, it is then possible to postulate that 2,4-hexadiene will predominate in the reaction products ; such a structure, apparently, is the most stable under the given conditions.* The hexadiene can also be formed via the addition of an acetylene molecule, chemically sorbed on the catalyst, to the semihydrogenated form of the acetylene dimer, with subsequent hydrogenation of the semihydrogenated acetylene trimer that arises here. The small amount of benzene that is found in the liquid products can be regarded as being due to the thermal polymerization of acetylene, proceeding to a very slight degree in the reaction zone.

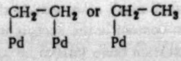
The reaction of the semihydrogenated form of acetylene with the hydrogen chemically sorbed on the catalyst yields ethylene, which will then hydrogenate further to ethane. However, in the presence of acetylene this reaction is highly improbable, since due to its greater unsaturation the acetylene will show better chemosorption than does ethylene [12] and will displace it from the catalyst surface. Despite this, the possibility is not excluded of small amounts of ethane arising in the presence of acetylene, due to reaction of the acetylene with the hydrogen of the ethylene particles that are formed on the catalyst before the latter are displaced from the surface.

With a large excess of hydrogen and under the influence of high temperatures the ethylene can show destructive hydrogenation to methane.



$$\underset{Pd}{CH_2}-\underset{Pd}{CH_2}+\underset{Pd}{4H} \rightarrow 6Pd + 2CH_4 \qquad (V)$$

Ethylene and its semihydrogenated form are not inclined to polymerize, since being adsorbed on the catalyst, they represent saturated compounds



$$\underset{Pd}{CH_2}-\underset{Pd}{CH_2} \text{ or } \underset{Pd}{CH_2}-CH_3$$

capable of reacting only with such highly active agents as the hydrogen that appears on the surface of a hydrogenation catalyst.

The reaction for the hydropolymerization of acetylene proceeds only on the surface of the palladium, on the atoms of which the formation of intermediate semihydrogenated particles occurs; consequently, the addition of polymerization agents (phosphoric acid, synthetic aluminosilicate, etc.) to the catalyst cannot exert any effect, which is borne out by the experimental data.

EXPERIMENTAL

1. Characterization of the Starting Products, Method of Operation and Analyses

The catalyst was prepared by depositing palladium chloride on clay, previously freed from iron impurities by repeated boiling with 20% hydrochloric acid.

Cylinder acetylene was purified from phosphine, ammonia and other impurities. The gas after purification contained 98-99.8% acetylene (remainder nitrogen), which was determined by absorption in an alkaline solution of mercurous cyanide [13].

Electrolytic hydrogen was used, and it was purified from oxygen traces by absorption in an alkaline pyrogallol solution [14].

Ethylene was obtained by the dehydration of ethyl alcohol, and after purification by passage through solid caustic and alkaline pyrogallol solution, analyzed 99% ethylene (by absorption in saturated bromine water).

Divinyl was isolated from the divinyl that was obtained as rectificate in the production of synthetic rubber by treating it with an ammoniacal solution of the acetate of cuprous oxide and subsequent desorption; it analyzed 95% divinyl (based on the weight of tetrabromide that was obtained by bromination [14]), the remaining 5% being pseudobutylene (2-butene).

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* For example, according to the data of R. Ya. Levina and coworkers, in the presence of catalysts 1,3-hexadiene is easily isomerized into 2,4-hexadiene [11].

The hydrogenation of acetylene was run in a quartz tube, filled with the catalyst and placed in an electrically heated tube furnace. Prior to experiment the catalyst was reduced in a hydrogen stream for 24 hours at 230°. The reaction products passed through a condenser, ice-cooled receiver, and a trap cooled with a mixture of alcohol and dry ice. The uncondensed gas was collected in a gasometer, filled with saturated salt solution. The condensate from the trap, composed chiefly of butylenes and divinyl, and also some dissolved ethylene acetylene, was distilled through a column of the Podbelniak type. The presence of propylene and butane in the reaction products could not be shown. The divinyl concentration was determined by the bromination method [14]. The total amount of divinyl and butylene was established by absorption in 84% sulfuric acid [14]. The amount of isobutylene was determined by the Deniges method [15]. The absence of vinylacetylene in the butylene-divinyl fraction (where it could be present) was established qualitatively by means of the Ilosov reagent. Ethane and methane were determined by fractional combustion over copper oxide and subsequent absorption of the resulting carbon dioxide in caustic solution [14].

The condensate from the receiver, representing the liquid products of the reaction, could not be studied after each experiment due to its small amount; consequently, for study we took the combined condensates of several experiments. The results of studying the liquid reaction products are given below.

2. Influence of Various Factors on the Process for the Catalytic Hydrogenation and Hydropolymerization of Acetylene

a) Influence of temperature. The experiments were run at 180-185, 335-340 and 440-450° and a contact time of about 2 seconds. The amount of hydrogen in the starting acetylene-hydrogen mixture was about 30%. The catalyst was palladium, deposited on clay in an amount of 1%. The experimental results are given in Table 1.

b) Influence of the palladium content in the catalyst. The experiments were run with catalyst specimens containing 0.1, 0.5, 1, 3 and 10% palladium on clay. The temperature was 335-350°, and the contact time varied from 1 to 2.2 seconds. The hydrogen concentration in the starting gas mixture was 33-33%. The experimental results are plotted in Fig. 1.

c) Influence of the initial hydrogen concentration. The experiments were run at 335-350° and a contact time of 1-1.3 seconds on a 1% palladium-on-clay catalyst. The experimental results are plotted in Fig. 2. The passage of acetylene alone over the catalyst with a contact time of 1.1 seconds failed to be accompanied by any change in either the composition or quantity of gas. We failed to detect the formation of vinylacetylene and liquid products.

d) Influence of the contact time. The experiments were run at 335-340°. The palladium content on the clay was 1%. The hydrogen concentration in the starting gas mixture was 30-33% in the first series of experiments, and 47.5-51% in the second series. The contact time, computed by the Hurd method [16], was varied from 3.4 down to 0.24 seconds. The results of the first series of experiments are plotted in Figs. 4 and 5. A similar set of data was obtained in the second series of experiments; for this reason the results of this series of experiments are not presented here.

3. Study of the Influence of Ethylene and Divinyl on the Acetylene Hydropolymerization Process

a) Hydrogenation of ethylene. The experiments were run at 340° and a contact time of about 1.5 seconds on a 1% palladium-on-clay catalyst. The hydrogen content in the starting ethylene-hydrogen mixture was 24 and 40 volume %. The conversion of the ethylene was not accompanied by the processes of polymerization and hydropolymerization. Only the hydrogenation products of ethylene were formed—ethane and a small amount of methane.

b) Hydrogenation of ethylene-acetylene mixtures. The temperature was 335-350°, the contact time 1.5-1.7 seconds, and the hydrogen concentration in the starting ethylene-acetylene mixture was about 34%. The catalyst was 1% palladium on clay. The experimental results are given in Table 2.

c) Hydrogenation of divinyl. The experiments were run at 340°, a contact time of 1.4-1.5 seconds and a hydrogen concentration in the starting gas mixture of about 38%. The catalyst was 1% palladium on clay. The main product obtained in the hydrogenation of divinyl was butylene. Butane was obtained in extremely small amounts.

d) Hydrogenation of divinyl in the presence of acetylene. The experiments were run at 340-350° and a contact time of 1-1.1 seconds. The catalyst was 1% palladium on clay. On the average, the starting gas mixture had the following composition (in %): hydrogen about 40, acetylene 45-50, divinyl 10-14, and butylene about 0.8. The experimental results are given in Table 3.

4. Study of the Composition of the Liquid Reaction Products.

From the liquid hydrocarbons, taken in an amount of 36.4 g, after drying over calcium chloride and distillation through a column, there was isolated 2.2 g of a fraction with b.p. 79-81.5° and n_D^{20} 1.4539. Literature for 2,4-hexadiene: b.p. 80-81° and n_D^{20} 1.4535 [17]. A part of this fraction was used to prepare the maleic anhydride derivative, using the method of Diels and Alder [18]. After recrystallization from ligroin the obtained product melted at 94°. According to the literature the melting point of the 2,4-hexadiene-maleic anhydride derivative is 95-96° [18].

Using the visual method of determining intensity, a study was made of the Raman spectra of the fraction with b.p. 79-81.5°. The spectral analysis data (in reciprocal centimeters) are:

603 (2), 835 (2), 850 (2), 889 (0.5), 938 (0.5), 991 (8), 1030 (0.5), 1150 (3), 1172 (5), 1220 (1), 1239 (5), 1280 (1), 1300 (5), 1380 (4), 1449 (4), 1552 (1), 1578 (1.5), 1605(1b db), 1623 (1), 1640 (4), 1655 (25), 1668 (5), 2856 (2), 2917 (3), 2936 (1), 3009 (0.5), 3064 (1), 3346 (2).

The presence of frequencies 603, 991, 1578 and 1605 cm^{-1} in the spectrum indicates the presence of benzene. The frequencies 1655 and 1668 cm^{-1}, and their strong intensity, indicate the presence of a conjugated system of double bonds. A comparison of the found frequencies with the frequencies 1656 and 1668 cm^{-1} in the spectrum for 2,4-hexadiene [19] leads to the conclusion that this hydrocarbon is present in the investigated fraction.[*]

SUMMARY

1. When acetylene is reacted with hydrogen in the presence of a palladium catalyst, simultaneously with the hydrogenation of acetylene to ethylene and ethane, and in part to methane, there proceeds hydrodimerization of acetylene to divinyl and n-butylene, and also its hydropolymerization to yield liquid products.

2. The fundamental characteristic of the investigated reaction is the impossibility of acetylene showing catalytic polymerization in the absence of hydrogen. The degree of acetylene conversion and the yield of hydrodimerization products are found to be closely related to the hydrogen content in the starting gas mixture.

3. Divinyl appears as the primary hydrodimerization product, and butylene as the secondary product.

4. In accord with the theory of the semihydrogenated state, a scheme was proposed for the catalytic hydropolymerization of acetylene under the influence of a palladium catalyst, explaining the formation of divinyl and butylenes and the discounting participation of hydrogen in the polymerization process.

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THE INHIBITED OXIDATION OF α-PINENE

E. N. Novikova

The purpose of this investigation is to study the influence of a number of inhibitors on the oxidation of terpenes and elucidate the relationship existing between the structure of inhibitors and their protective properties.

It is known [1] that bicyclic terpenes are easily changed, undergoing transformation into either monocyclic compounds or into bicyclic compounds of different structure. Thus, α-pinene under the influence of various substances and reaction conditions gives extremely diverse products. When oxidized with atmospheric oxygen it is converted into tarry substances. It is believed [2] that the probable products of the autocatalytic oxidation of terpenes with oxygen are compounds of peroxide character. According to contemporary theories α-pinene first forms the peroxide, and then the oxide (pinol), which, suffering hydration, gives the glycol—sobrerol. When α-pinene is oxidized with hydroperoxides the oxidation proceeds at the double bonds, as the result of which oxides are obtained [3].

The studies of other investigators [4,5] have shown that the action of oxygen on hydrocarbons is a free-radical chain reaction, as a result of which hydroperoxides are formed. Suffering decomposition, the hydroperoxides can either initiate or terminate the reaction chain. Effective inhibitors show a great influence on the termination of the reaction chain. It was established [6, 7] that the inhibitor is consumed in the oxidation process by reacting with the peroxide radicals of the hydrocarbon and in that way suppressing the oxidation reaction. Small amounts of an effective inhibitor can strongly retard the chain reaction, showing very rapid progress in the absence of an inhibitor.

A study of the oxidation of α-pinene in the presence of inhibitors can offer interesting material from the viewpoint of preventing the oxidation of terpenes by atmospheric oxygen during storage and in processing. From a different viewpoint, a study of the oxidation of α-pinene is of great interest for the reason that in its structure it is a substance close to rubber and can serve as a model for it. At high temperatures α-pinene, the same as other terpenes, gives isoprene [1], which appears as the fundamental structural unit of rubber. In addition, when studying the protective properties of inhibitors on rubber films an important phase in the correct evaluation of inhibitors is their solubility in rubber [8]. In the oxidation of terpenes a dissolved amount of inhibitor can be introduced, which permits making a more valid comparison of different inhibitors based on their degree of protective action against oxidation as a function of the structure and polarity of their molecules.

EXPERIMENTAL

To study the influence shown by the character and position of functional groups in inhibitor molecules on their protective properties we took phenols, naphthalene derivatives and diphenylamine, which were carefully purified by either recrystallization or distillation. For the naphthalene derivatives and diphenylamine the amounts of inhibitor taken were calculated on the basis of 2 mmole of inhibitors per mole of α-pinene; due to their low solubility the phenols were taken in the amount of 0.5 mmole per mole of α-pinene. The latter was isolated from spirits of turpentine and was distilled twice through a 2 m rectification column packed with aluminum rings: b.p. 155-156°, d_4^{20} 0.8599, n_D^{20} 1.4659; nitrosochloride: m.p. 103.5°.

A semivacuum apparatus was used for the inhibited oxidation of α-pinene, consisting of a manometer, burette and an oxygen supply source. Mercury in the burette served as a liquid seal. Since mercury vapors exert an inhibiting influence [9] on the oxidation process, an absorber made of gilded asbestos was inserted in the system ahead of the reaction vessel. The oxidation at 80° was run with dry molecular oxygen in special

TABLE 1

Degree of Oxidation Shown by α-Pinene at 80° in the Presence of Inhibitors for Atmospheric Oxygen

Name of inhibitor	Melting point of inhibitor	Percent oxygen absorbed by 1 mole of α-pinene in 7 hours	Name of inhibitor	Melting point of inhibitor	Percent oxygen absorbed by 1 mole of α-pinene in 7 hours
Without inhibitor	—	29.5	Diphenylamine	52°	2.7
β-Naphthylamine	110.5°	10.8	p-Hydroxydiphenylamine	69	0.17
α-Nitroso-β-naphthol	108	1.42	1,4-Diphenylphenylenediamine	137	0.06
Phenyl-β-naphthylamine (Neozone D)	107.5	1.00	Phloroglucinol	208	23
β-Naphthol	122.3	0.72	Resorcinol	108	16.9
Phenyl-α-naphthylamine (Neozone A)	62	0.19	Hydroquinone	170	5.5
			Pyrocatechol	104	0
p-Hydroxyphenyl-β-naphthylamine (Hydroxyneozone D)	126.7	0	Pyrogallol	132.5	0.08

vessels equipped with external water heat and an ultrathermostat. To assure uniform oxidation throughout the whole volume, the α-pinene was constantly stirred by means of a magnetic stirrer. All of the oxidation experiments were run at a constant oxygen pressure of 755 mm. The oxidation rate was determined from the amount of oxygen absorbed by 0.025 mole of α-pinene in known time intervals. The volume of oxygen absorbed (NTP) was expressed in milliliters per mole of α-pinene. The experimental results obtained for the oxidation of α-pinene, both in the absence and presence of inhibitors, are summarized in Tables 1 and 2 and plotted in Figs. 1-5. If it is assumed that 1 mole of oxygen is added in the complete oxidation of 1 mole of α-pinene, it then becomes possible to calculate the degree of oxidation (expressed in percent oxygen absorption) shown by α-pinene in the presence of inhibitors.

The degree of oxidation shown by α-pinene after its oxidation for 7 hours in the presence of inhibitors is given in Table 1. The degree of oxidation incurred in 7 hours in the presence of inhibitors can be calculated if the amount of oxygen absorbed by pure α-pinene in the same length of time is taken as 100%. The experimental results, given in Table 1, represent definite interest from the viewpoint of comparing the protective activity shown by different groups of antioxidants and individual compounds in the oxidation of α-pinene with atmospheric oxygen.

Naphthalene derivatives. The curves in Fig. 1 show the kinetics for the oxidation of α-pinene with oxygen in the presence of naphthalene derivatives. The oxygen temperature, pressure and concentration, influencing both the oxidation rate and the magnitude of the induction period, were maintained constant in our experiments. Consequently, the observed retardation of the process for the oxidation of α-pinene by oxygen can be explained as due to the action of inhibitors. Some of them reduce the oxidation rate to variable degree, while others increase the duration of the induction period. As the experimental data show, based on the vigor of protective action shown toward the oxidation of α-pinene by oxygen, the antioxidants of this group can be arranged in the following order: p-hydroxyphenyl-β-naphthylamine > phenyl-α-naphthylamine > β-naphthol > phenyl-β-naphthylamine > α-nitroso-β-naphthol > β-naphthylamine.

To considerable degree the inhibition effectiveness is determined by the antioxidant concentration in the reaction mixture. Since equimolar amounts of inhibitors were studied in the present experiments, the different degree of α-pinene protection shown by the indicated antioxidants can be explained by their different chemical nature.

A comparison of the inhibitory activity (based on the amount of oxygen absorbed by α-pinene) shown by β-naphthylamine and β-naphthol (Fig. 1) reveals that replacement of the hydrogen in naphthalene by a hydroxyl group gives a substance with a higher antioxidant action than when the replacing substituent is the amino group. For all practical purposes β-naphthylamine is a poor inhibitor for the oxidation of α-pinene, which we had shown earlier in the inhibited oxidation of dipentene [10]. Although the rate for the oxidation of α-pinene in the presence of β-naphthylamine is lower than for pure pinene, still it shows constant increase, which, it must be assumed, is associated with the weak disturbance of the chain process by β-naphthylamine.

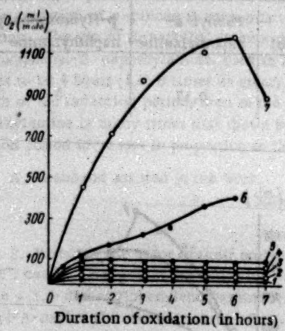

Fig. 1. Influence of naphthalene derivatives on the oxidation of α-pinene.
1) p-hydroxyphenyl-β-naphthylamine, 2) phenyl-α-naphthylamine, 3) β-naphthol, 4) phenyl-β-naphthylamine, 5) α-nitroso-β-naphthol, 6) β-naphthylamine, 7) α-pinene.

Both p-hydroxyphenyl-β-naphthylamine and phenyl-α-naphthylamine show a very high degree of effectiveness in protecting α-pinene from oxidation. Oxygen absorption failed to be observed when α-pinene was subjected to oxidation at 80° for 12 hours in the presence of p-hydroxyphenyl-β-naphthylamine. The high inhibitory activity shown by p-hydroxyphenyl-β-naphthylamine when compared with phenyl-β-naphthylamine is evidently due to the introduction of a hydroxyl group, which changes the polarity of the molecule and possibly, as had been established earlier [11] for rubber, the ability to react with the peroxides formed in the oxidation process.

Phenyl-α-naphthylamine shows a stronger antioxidant action than does phenyl-β-naphthylamine. Here the position occupied by a substituent shows its influence, and specifically, an inhibitor with substitution in the α-position is more active than one with substitution in the β-position, which had been observed by many investigators for rubber and for oils.

At first the process for the oxidation of pure α-pinene proceeds at an increasing rate, reaches a maximum, and then at a decreasing rate. In the presence of the antioxidants indicated in Table 2 an increase in the rate of α-pinene oxidation fails to be observed in 10 hours. The oxygen is absorbed at a constant rate, characteristic for each inhibitor.

Diphenylamine derivatives. The hindering action shown by diphenylamine in the oxidation of rubber, oils and divinylacetylene has been disclosed by a number of investigators [11-13]. The behavior of diphenylamine and its derivatives in the oxidation of α-pinene deserves definite interest. We studied diphenylamine, -hydroxydiphenylamine and 1,4-diphenylphenylenediamine. As can be seen from the curves for the kinetics of α-pinene oxidation (Fig. 2), the mentioned inhibitors show an antioxidant action. However, p-hydroxydiphenylamine shows considerably more activity than does diphenylamine, which is explained by the presence, together with the NH group, of a hydroxyl group. 1,4-Diphenylphenylenediamine shows even greater activity, evidently due to the hydrogens found on the two secondary amine groups. But the highest antioxidant action is shown by p-hydroxyphenyl-β-naphthylamine (Table 2), which must be assumed to be associated with making the molecule more complicated, as had been established for a number of inhibitors in the oxidation of rubber [9].

Phenols. The protective action shown by dihydroxybenzenes and trihydroxybenzenes was studied. It was found that for all practical purposes phloroglucinol and resorcinol (Fig. 3) fail to inhibit the oxidation of α-pinene. On the contrary, pyrocatechol and pyrogallol suppress oxidation completely. In their antioxidant action hydroxyhydroquinone and hydroquinone are intermediate between the first and second. A similar behavior by phenols, as we had shown earlier, was observed in the oxidation of solutions of rubber and of dipentene [10,14]. As a result, the phenols with a hydroxyl group in the ortho position (pyrogallol and pyrocatechol) are the most active inhibitors. In hydroxyhydroquinone the protective action is weakened, probably due to the influence of the hydroxyl group in the para position. The meta-isomers of phenols are practically without inhibitory effect in the oxidation of α-pinene. Indications for analogous behavior of phenols in the oxidation of other substances are encountered in the earlier studies of a number of authors.

Influence of inhibitor concentration. The effect of the antioxidant action shown by inhibitors depends on their concentration. Since 0.5 mmole of either resorcinol or phloroglucinol proved to be insufficient for retarding the oxidation of α-pinene, we ran the oxidation at higher resorcinol concentrations. As can be seen from the curves in Fig. 4, an increase in the resorcinol concentration to 2 mmole does increase its antioxidant action, but it still remains less effective than was observed for the other phenols examined above. As regards p-hydroxy-

TABLE 2

Average Rate for the Absorption of Oxygen by α-Pinene at 80° in the Presence of Inhibitors and for a Period of 10 Hours.

Name of Inhibitor	α-Nitroso-β-naphthol	Phenyl-β-naphthylamine	β-Naphthol	Phenyl-α-naphthylamine	p-Hydroxyphenyl-β-naphthylamine
O_2 (ml/mole/minute).	0.70	0.50	0.34	0.17	0

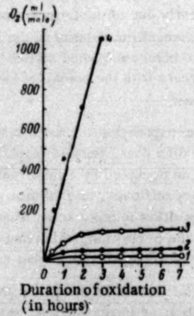

Fig. 2. Influence of diphenylamine derivatives on the oxidation of α-pinene.
1) 1,4-diphenylphenylenediamine, 2) p-hydroxydiphenylamine, 3) diphenylamine, 4) α-pinene.

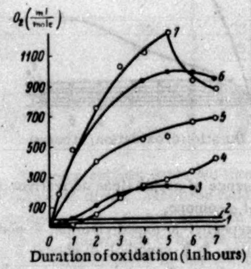

Fig. 3. Influence of phenols on the oxidation of α-pinene.
1) pyrocatechol, 2) pyrogallol, 3) hydroquinone, 4) hydroxyhydroquinone, 5) resorcinol, 6) phloroglucinol, 7) α-pinene.

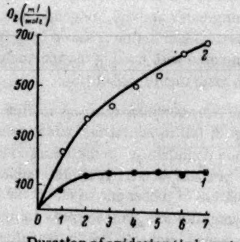

Fig. 4. Influence of resorcinol concentration on the oxidation of α-pinene.
1) 2 mmole resorcinol, 2) 0.5 mmole resorcinol.

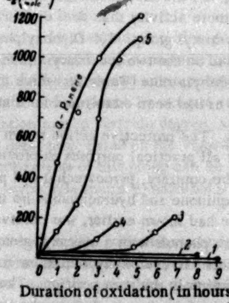

Fig. 5. Influence of p-hydroxyphenyl-β-naphthylamine concentration on the oxidation of α-pinene.
1) 2 mmole, 2) 0.5 mmole, 3) 0.1 mmole, 4) 0.05 mmole, 5) 0.01 mmole.

phenyl-β-naphthylamine, when using it at a concentration of 2 mmole and running the experiment for 10 hours, we were unable to establish the length of the induction period; for this reason we studied the influence of p-hydroxyphenyl-β-naphthylamine concentration on its behavior as an inhibitor. A comparison of the kinetics curves in Fig. 5 permits the observation that the protective action shown by p-hydroxphenyl-β-naphthylamine in the oxidation of α-pinene is very great: even 0.01 mmole of the given inhibitor retards the chain oxidation reaction. The use of β-naphthol in an amount of 2 mmole gives a 30-minute induction period, while for p-hydroxyphenyl-β-naphthylamine, used in an amount of 0.1 mmole (i.e. 1/20 as much), the induction period proves to be 4 hours (i.e. 8 times as great). As a result, if the protective action of an inhibitor is judged by the length of the induction period, then in the oxidation of α-pinene the activity shown by p-hydroxyphenyl-β-naphthylamine is many times that shown by β-naphthol. At low inhibitor concentrations the length of the induction period increases in proportion to the inhibitor concentration.

A. Ritenband assisted in the work.

SUMMARY

1. Based on the vigor of their protective action, the inhibitors for the oxidation of α-pinene by oxygen (at 80°) can be arranged in the following order: pyrocatechol > pyrogallol > p-hydroxyphenyl-β-naphthylamine > 1,4-diphenylphenylenediamine >p-hydroxydiphenylamine > phenyl-α-naphthylamine > β-naphthol > phenyl-β-naphthylamine > α-nitroso-β-naphthol >diphenylamine β-naphthylamine.

2. The meta-isomers of phenols (resorcinol and phloroglucinol) are weaker oxidation inhibitors than are the para-isomers (hydroquinone and hydroxyhydroquinone).

3. With the exception of β-naphthylamine, naphthalene derivatives are active oxidation inhibitors.

4. The secondary amines show an increase in protective properties when a hydroxyl group is introduced into their molecule (p-hydroxydiphenylamine, p-hydroxyphenyl-β-naphthylamine).

5. The amino and hydroxy derivatives of naphthalene (β-naphthol and β-naphthylamino) show different activity as oxidation inhibitors.

6. Within the limits of a group the inhibitor structure possesses significance, influencing both hydrogen mobility (a factor leading to rupture of the oxidation chain) and the polarity (secondary factor), leading to a shielding of the double bonds.

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THE REACTIONS FOR THE FORMATION OF POLYORGANOSILOXANES BY THE HETEROFUNCTIONAL CONDENSATION METHOD

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It is known that the treatment of alkyl(aryl)halosilanes and other compounds, showing substitution of water-hydrolyzable groups on the silicon atom, leads to the formation of products that are easily transformed into high-molecular compounds—the polyorgansiloxanes. The heating of alkyl(aryl)acetoxysilanes can also yield similar polymers; here the acetate groups are cleaved with the formation of acetic anhydride and polyorganosiloxanes [1]. It has been indicated in the patent literature that the heating of mixtures of alkyl(aryl)chlorosilanes with alkyl(aryl)ethoxysilanes in the presence of either $AlCl_3$ or $FeCl_3$ results in the evolution of ethyl chloride and the formation of resins [2].

We investigated the reaction of alkyl(aryl)acetoxysilanes with alkyl(aryl)halosilanes and with alkyl(aryl)-ethoxysilanes and found that condensation occurs when the indicated compounds are heated in the presence of catalysts to give polyorganosiloxanes and the evolution of acetyl chloride in the first case, and of ethyl acetate in the second.

A study of the condensation of alkyl(aryl)acetoxysilanes with alkyl(aryl)chlorosilanes revealed that the amount of acetate groups and the chlorine content in the reaction medium during the heating process decrease in proportion to the amount of acetyl chloride evolved in the reaction process. Thus, for example, in the heating of equimolar amounts of dimethyldiacetoxysilane and phenyltrichlorosilane at 140° in the presence of $FeCl_3$ both the chlorine content and the amount of acetate groups show a sharp drop, especially at the start of heating, while the amount of acetyl chloride evolved here shows an increase (Fig. 1).

A similar reaction is observed in the heating of equimolar amounts of methylphenyldiacetoxysilane and phenyltrichlorosilane (Fig. 2); here in both the first and second cases the viscosity of the products increases during the heating process.

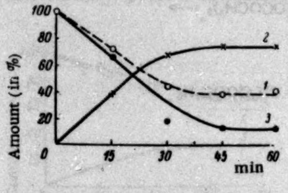


Fig. 1. Change in the amount of CH_3COO (1), Cl (3) and amount of formed CH_3COCl (2) in the reaction of dimethyldiacetoxysilane with phenyltrichlorosilane.

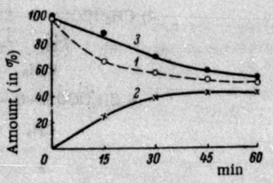
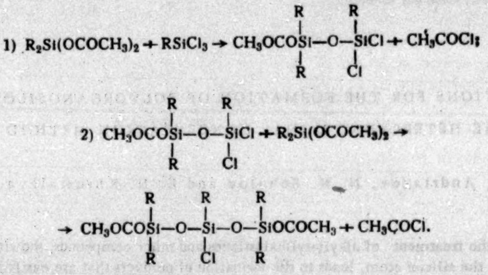


Fig. 2. Change in the amount of CH_3COO (1), Cl(3) and amount of formed CH_3COCl (2) in the reaction of methylphenyldiacetoxysilane with phenyltrichlorosilane.

These data show that the heating of alkyl(aryl)acetoxysilanes with phenyltrichlorosilanes in the presence of ferric chloride results in stepwise condensation, which leads to the formation of polyorganosiloxanes in accord with the scheme.



$$1)\ R_2Si(OCOCH_3)_2 + RSiCl_3 \rightarrow CH_3OCO\underset{R}{\overset{R}{Si}}-O-\underset{Cl}{\overset{R}{Si}}Cl + CH_3COCl;$$

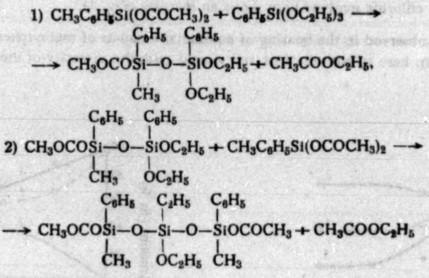
$$2)\ CH_3OCO\underset{R}{\overset{R}{Si}}-O-\underset{Cl}{\overset{R}{Si}}Cl + R_2Si(OCOCH_3)_2 \rightarrow$$

$$\rightarrow CH_3OCO\underset{R}{\overset{R}{Si}}-O-\underset{Cl}{\overset{R}{Si}}-O-\underset{R}{\overset{R}{Si}}OCOCH_3 + CH_3COCl.$$

The subsequent process is accompanied by the obtained products condensing among themselves and with the monomers until complex polymeric molecules are formed; in this connection it should be mentioned that the reaction fails to go to completion, and a part of the acetate groups and chlorine remains in the polymer; this indicates that the condensation reaction is practically terminated when a higher viscosity is attained.

The heating of equimolar amounts of methylphenyldiacetoxysilane and phenyltriethoxysilane also results in condensation, which is accompanied by a change in the amounts of ethoxyl and acetate groups during heating in proportion to the evolution of ethyl acetate (Fig. 3).

These data, and also the viscosity increase shown by the reaction product, reveal that condensation takes place between methylphenyldiacetoxysilane and phenyltriethoxysilane, which in general form can be depicted as follows:



$$1)\ CH_3C_6H_5Si(OCOCH_3)_2 + C_6H_5Si(OC_2H_5)_3 \longrightarrow$$

$$\longrightarrow CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}-O-\underset{OC_2H_5}{\overset{C_6H_5}{Si}}OC_2H_5 + CH_3COOC_2H_5,$$

$$2)\ CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}-O-\underset{OC_2H_5}{\overset{C_6H_5}{Si}}OC_2H_5 + CH_3C_6H_5Si(OCOCH_3)_2 \longrightarrow$$

$$\longrightarrow CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}-O-\underset{OC_2H_5}{\overset{C_2H_5}{Si}}-O-\underset{CH_3}{\overset{C_6H_5}{Si}}OCOCH_3 + CH_3COOC_2H_5$$

etc.

For all practical purposes the above reactions fail to proceed in the absence of catalysts, for example, after heating for 4 hours at 60-120°.

We took ferric chloride (both anhydrous and hydrated) and aluminum chloride as catalysts. As was experimentally shown, these catalysts fail to show any influence on the individual reaction components even after 4-hour heating at 140°.

The experimental results of comparing ferric chloride and aluminum chloride as catalysts in the condensation of dimethyldiacetoxysilane with phenyltrichlorosilane are given in Table 1.

TABLE 1

Ferric Chloride and Aluminum Chloride as Catalysts in the Condensation of Dimethyldiacetoxysilane with Phenyltrichlorosilane

Expt. Nos.	Ferric chloride (or $AlCl_3$) (in %)	Reaction temperature	Amount of acetyl chloride evolved (in % of theoret.)	Amount of silicon in the volatiles (in %)	Amount (in %)			Amount of Cl (in %)		
					CH_3COO in the starting mixture	CH_3COO in the the final product	CH_3CO in volatiles	In the starting mixture	in the final product	in the volatiles
1	0.1	120°	53.3	Traces	34.35	27.96	36.41	23.27	12.17	49.68
2	0.5	110-115	66.6	2.43	34.35	18.18	47.62	23.66	9.44	45.64
3	1.0	105	87.1	2.02	34.35	9.39	54.58	24.16	5.68	44.21
4	0.1 $AlCl_3$	120	56.4	16.97	34.35	43.10	11.69	23.27	9.11	46.00

With increase in the catalyst amount from 0.1 to 1.0% the reaction temperature decreases, condensation is more profound, as a result of which more volatiles are evolved, and the amounts of acetate groups and chlorine in the condensation product show decrease. An examination of the analysis results reveals that the amount of acetyl groups (with the exception of Expt. 3, Table 1) in the volatile products (acetyl chloride) fails to correspond with theory (54.84%). A larger amount of acetate groups is present in the condensation products than should prevail for a given degree of condensation, based on the amount of chlorine in the product. Thus, for example, in Expt. 1, for a chlorine content of 12.17% in the condensation product the amount of acetate groups should be 18.0%,and instead it is 27.96%. This phenomenon is explained by the fact that acetyl chloride reacts with dimethyldiacetoxysilane to yield dimethyldichlorosilane and acetic anhydride [3]. The acetic anhydride, boiling at 140°, remains in the condensation products, while the dimethyldichlorosilane, boiling at 70°, escapes with the volatiles; the latter compound is responsible for the presence of silicon in the volatile products and the increased chlorine content. In the presence of aluminum chloride this reaction shows more active progress. In the presence of 1% ferric chloride (Expt. 3) the reaction proceeds at 105°, and the analysis results practically coincide with the theoretical values.

When methylphenyldiacetoxysilane is reacted with phenyltrichlorosilane (Fig. 2) the final reaction products contain acetate groups and chlorine in nearly equivalent amounts. Here the methylphenyldichlorosilane, formed under catalyst action, remains in the reaction products, since it boils at 204°. In like manner, the final reaction product in the reaction of dimethyldiacetoxysilane with phenyltriethoxysilane at 100° (Fig. 3) contains acetate and ethoxyl groups in equivalent amounts.

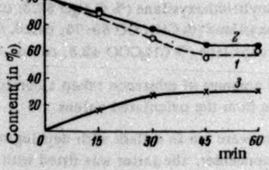


Fig. 3. Change in the amount of CH_3COO (1), C_2H_5O (2) and amount of formed $CH_3COOC_2H_5$ (3) in the reaction of dimethyldiacetoxysilane with phenyltriethoxysilane.

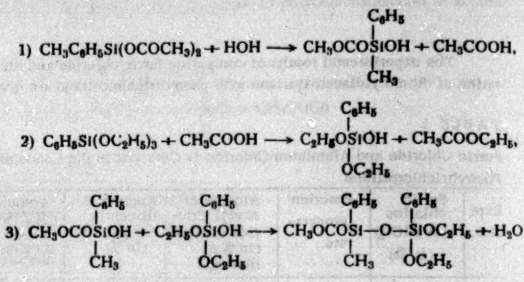
The condensation of methylphenyldiacetoxysilane with phenyltriethoxysilane at 160° results in thermal decomposition of the acetates with the formation of acetic anhydride and polyorganosiloxanes, as a result of which the reaction product contains an excess of acetate groups.

All of these data show that the examined condensation reactions should be run at temperatures of the order of 100-110° in the presence of ferric chloride as catalyst. Hydrated ferric chloride facilitates more rapid reaction. This is probably due to the positive influence of water on the process, which can be seen if we assume the following mechanism for the reactions:

TABLE 2

Reaction Conditions and Results of the Experiments on the Condensation of Acetoxy-ethoxy-chloro-organosilanes

Figure No.	Reaction components: dimethyldiacetoxysilane, mole	dimethyldiacetoxysilane, g	methylphenyldiacetoxysilane, mole	methylphenyldiacetoxysilane, g	phenyltrichlorosilane, mole	phenyltrichlorosilane, g	phenyltriethoxysilane, mole	phenyltriethoxysilane, g	Reaction temperature	Weight of final product (in g)	Weight of volatiles (in g)	Amount of volatiles (in %): CH_3CO found	CH_3CO calc.	Cl found	Cl calc.	C_2H_5O found	C_2H_5O calc.
1	0.45	79.2	–	–	0.3	63.3	–	–	95°	89.0	52.7	50.2	54.84	44.1	45.18	–	–
2	–	–	0.15	40.9	0.1	21.2	–	–	120-130	48.0	10.0	55.0	54.84	39.39	45.18	–	–
3	0.15	96.4	–	–	–	–	0.1	25.8	120	32.0	8.6	45.2	48.8	–	–	39.0	51.1

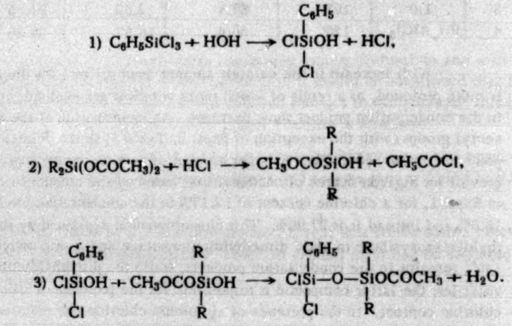


$$1)\ CH_3C_6H_5Si(OCOCH_3)_2 + HOH \longrightarrow CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}OH + CH_3COOH,$$

$$2)\ C_6H_5Si(OC_2H_5)_3 + CH_3COOH \longrightarrow C_2H_5O\underset{OC_2H_5}{\overset{C_6H_5}{Si}}OH + CH_3COOC_2H_5,$$

$$3)\ CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}OH + C_2H_5O\underset{OC_2H_5}{\overset{C_6H_5}{Si}}OH \longrightarrow CH_3OCO\underset{CH_3}{\overset{C_6H_5}{Si}}{-}O{-}\underset{OC_2H_5}{\overset{C_6H_5}{Si}}OC_2H_5 + H_2O.$$

or



$$1)\ C_6H_5SiCl_3 + HOH \longrightarrow Cl\underset{Cl}{\overset{C_6H_5}{Si}}OH + HCl,$$

$$2)\ R_2Si(OCOCH_3)_2 + HCl \longrightarrow CH_3OCO\underset{R}{\overset{R}{Si}}OH + CH_3COCl,$$

$$3)\ Cl\underset{Cl}{\overset{C_6H_5}{Si}}OH + CH_3OCO\underset{R}{\overset{R}{Si}}OH \longrightarrow Cl\underset{Cl}{\overset{C_6H_5}{Si}}{-}O{-}\underset{R}{\overset{R}{Si}}OCOCH_3 + H_2O.$$

Here the catalyst shows a postive influence on the third step of the reaction and retains the water, making its removal from the reaction difficult.

EXPERIMENTAL

In our work we used dimethyldichlorosilane (% Cl 55.0; calcd. 54.98), methyltrichlorosilane (% Cl 70.5; calcd. 71.19), phenyltrichlorosilane (% Cl 50.2; calcd. 50.31), methylphenyldichlorosilane (% Cl 33.8; calcd. 37.17), phenyltriethoxysilane (% C_2H_5O 52.3; calcd. 56.25), dimethyldiacetoxysilane (% CH_3COO 69-70; calcd. 67.04) and methylphenyldiacetoxysilane (% CH_3COO 42.8; calcd. 49.57).

In calculating the amounts of substance taken a correction was introduced for deviations from the calculated values.

All of the reactions were run in a flask with dephlegmator, connected to a straight condenser; the latter was fitted with a cooled receiver and calcium chloride tube. The catalyst used was either anhydrous or hydrated (Experiments in Table 2) ferric chloride, taken in 1% amount based on the weight of starting products. The amounts of acetate groups and chlorine in the starting mixture were determined. Then the flask was heated and after the start of reaction samples were taken at 15 minutes intervals for analysis. The duration of reaction was 1 hour.

The results of some typical condensation reactions are given in Table 2; the reaction kinetics is given in Figs. 1-3. The acetate and acetyl groups were determined by titration with alkali and calculated on the basis of discounting the amount of chlorine determined by the Volhard method. When both acetate and ethoxyl groups were present in the product the first were determined by saponification with 0.5N alkali, and the second by the Zeisel method. In Figs. 1-3 the content of functional groups (Cl, C_2H_5O, CH_3COO) is plotted along the ordinate axis, taking their initial amount as 100%.

SUMMARY

1. The thermal condensation reactions of dimethyldiacetoxysilane and methylphenyldiacetoxysilane with phenyltrichlorosilane and phenyltriethoxysilane in the presence of catalysts were studied.

2. Polyorganosiloxanes are formed in the condensation reactions with the evolution of volatile products—respectively acetyl chloride and ethyl acetate.

3. A good catalyst for the reaction is ferric chloride; the optimum temperature for the reaction is 100-110°.

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THE REACTION OF TETRASUBSTITUTED SILANES WITH CARBON TETRACHLORIDE

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The free-radical reactions of CCl_4 with organoelement compounds are initiated by UV-light and organic peroxides. In both cases the CCl_4 gives radicals, which can then react differently, as, for example, in the reaction with diphenylmercury:

$$(C_6H_5)_2Hg + CCl_4 \xrightarrow{h\nu} C_6H_5HgCl + C_6H_5Cl + C_2Cl_6 [1].$$

$$(C_6H_5)_2Hg + CCl_4 \xrightarrow[\text{Peroxide}]{} C_6H_5CCl_3 + C_6H_5HgCl + C_2Cl_6 [2].$$

The reactions of CCl_4 with saturated hydrocarbons proceed somewhat differently. In this case H is ruptured from a carbon atom, first from a tertiary carbon, and replaced by chlorine. For example, the reaction of CCl_4 with isobutane gives tertiary butyl chloride.

$$(CH_3)_3CH + CCl_4 \xrightarrow{\text{Peroxide}} CHCl_3 + (CH_3)_3CCl [3].$$

The organoelement compounds of the fourth group $(C_6H_5)_4Pb$ and $(C_6H_5)_4Sn$ react differently with CCl_4: here cleavage of a radical occurs, the same as occurred with the organometallic compounds of mercury:

$$(C_6H_5)_4Pb + CCl_4 \rightarrow (C_6H_5)_2PbCl_2 + C_6H_5Cl + C_2Cl_6 [4].$$

The reactions of CCl_4 with organic compounds of germanium and silicon have not been studied.

As our study subject we selected the tetrasubstituted compounds of silicon $(C_2H_5)_4Si$, $CH_3Si(C_6H_5)_3$ and $(C_6H_5)_4Si$. The last two compounds when illuminated with UV-light fail to react with CCl_4. In the photoreaction of CCl_4 with $(C_2H_5)_4Si$ chlorination proceeds without cleavage of radical, i.e. it is analogous to the reaction of CCl_4 with the saturated hydrocarbons:

$$(C_2H_5)_4Si + CCl_4 \rightarrow C_2H_4ClSi(C_2H_5)_3 + CHCl_3;\ CHCl_3 + CCl_4 \rightarrow HCl + C_2Cl_6.$$

After illuminating a mixture of CCl_4 and $(C_2H_5)_4Si$ with UV-light for 160 hours we isolated chloroethyltriethylsilane from the reaction mixture. It is possible to form the α and β-isomers of this compound. It was shown that in the main the α-isomer is obtained, as proof of which is the absence of reaction with alcholic alkali solution and aqueous $AgNO_3$ solution even when heated. This type of chlorination reaction was observed by S. N. Ushakov and A. M. Itenberg [5] when $(C_2H_5)_4Si$ was chlorinated in the presence of 1-2% PCl_5. They obtained a mixture of the α- and β-isomers of chloroethyltriethylsilane, containing chiefly the α-isomer. Whitmore and Sommer [6], who ran the chlorination of $(C_2H_5)_4Si$ with sulfuryl chloride in the presence of benzoyl peroxide, also obtained the α-triethylchlorosilane. It is possible that both products are formed when a mixture of CCl_4 and $(C_2H_5)_4Si$ is illuminated with UV-light, but then the β-isomer decomposes. Actually, when a mixture containing α- and β-chloroethyltriethylsilanes was illuminated with UV-light the amount of β-isomer decreased, and a tarry residue was formed when the reaction mixture was distilled.

To initiate the reaction of CCl_4 with organosilicon compounds we examined, besides the action of light, also benzoyl peroxide and acetyl peroxide. Only the acetyl peroxide initiated the reaction of CCl_4 with $(C_2H_5)_4Si$. When heated, the reaction mixture evolved HCl and chloroethyltriethylsilane was obtained. In contrast to the photochemical reaction, a mixture of the α- and β-isomers was obtained. The presence of the β-isomer of chloroethyltriethylsilane was shown by HCl-cleavage reactions. In addition to C_2Cl_6, $CHCl_3$ was found in the reaction products.

EXPERIMENTAL

$(C_6H_5)_4Si$ was obtained by the Polis method [7]; $CH_3Si(C_6H_5)_3$ was synthesized by the reaction of C_6H_5Li with CH_3SiCl_3; $(C_2H_5)_4Si$ was synthesized through the organomagnesium compound [5]; CCl_4 was purified in the usual manner, b.p. 76-77°, n_D^{17} 1.4630.

A PRK-2 mercury quartz lamp served as the source of UV-light for running the photoreactions. Illumination of the reaction mixture was run in quartz test tubes at a distance of 15-20 cm from the light source, here the temperature of the reaction mixture was 35-40°. A trap containing solid NaOH was placed in the quartz test tube to absorb any evolved HCl. After reaction the amount of evolved HCl was determined. The reaction of CCl_4 with $(C_2H_5)_4Si$, initiated by acetyl peroxide, was run at the boiling point of CCl_4. A system of traps was connected to the condenser to absorb the HCl. The amount of peroxide, entering into reaction, was determined iodometrically. The total amount of chlorine in the chloroethyltriethylsilane was determined by decomposing known weights of the substance with metallic sodium in sealed ampuls at 400-450° and subsequent gravimetric determination of Cl^-, while the easily cleaved chlorine was determined by treating the analyzed substance with 0.5N alcholic KOH solution.

Reaction of $(C_6H_5)_4Si$ with CCl_4. A reaction mixture of 4 g of $(C_6H_5)_4Si$ and 30 g of CCl_4 was exposed to UV-illumination for 160 hours. We isolated unreacted CCl_4, b.p. 76-77°, n_D^{17} 1.4630, and $(C_6H_5)_4Si$, m.p. 227°.

Reaction of $CH_3Si(C_6H_5)_3$ with CCl_4. A reaction mixture of 2 g of $CH_3Si(C_6H_5)_3$ and 10 g of CCl_4 was exposed to UV-illumination for 160 hours. We isolated unreacted CCl_4, b.p. 76-77°, n_D^{17} 1.4630 and $CH_3Si(C_6H_5)_3$, m.p. 67°.

Reaction of $(C_2H_5)_4Si$ with CCl_4 I. A reaction mixture of 14 g of $(C_2H_5)_4Si$ and 15 g of CCl_4 was exposed to UV-illumination for 160 hours. The combined reaction mixture of three experiments was distilled through a fractionation column. The weight of the mixture taken was 83 g. The following fractions were obtained: 1) 76-77°, 30.5 g, n_D^{17} 1.4630, CCl_4; 2) 78-100°, 6.3 g; 3) 100-150°, 4.5 g, mixture CCl_4 and $(C_2H_5)_4Si$; 4) 151-154°, 20.3 g, n_D^{17} 1.4262, $(C_2H_5)_4Si$. The residue in the flask, weighing 18 g, was treated with 0.1N $AgNO_3$ solution to remove HCl, and here 0.1376 g of AgCl was isolated. The residual liquid was subjected to repeated vacuum distillation to remove C_2Cl_6 and isolate the pure products. Eight grams of the investigated liquid remained for the final distillation, from which the following fractions were collected: 1) 55-60° (9 mm), 4 g, n_D^{17} 1.4301, chlorine content 5%, residue probably $(C_2H_5)_4Si$ with C_2Cl_6 as impurity; 2) 67-72° (9 mm), 2.5 g, n_D^{17} 1.4507, d_{20}^{20} 0.9202, α-chloroethyltriethylsilane.

Found %: Cl total 20.23; hydrolyzable Cl 2.30; C 53.56; H 10.58; Si 15.88. M 180. Calculated %: Cl 19.88; C 53.78; H 10.64; Si 15.69. M 178.5.

II. A reaction mixture of 19 g of $(C_2H_5)_4Si$ and 30 g of CCl_4 was exposed to UV-illumination for 160 hours, and then vacuum distilled without prior treatment with 0.1N $AgNO_3$ solution. Here we isolated 1.03 g of a fraction with b.p. 75-80° (7 mm) and n_D^{17} 1.4610. Found %: hydrolyzable Cl 19.38; C 49.53; H 9.46. This fraction is possibly β-chloroethyltriethylsilane with C_2Cl_6 as impurity. The freezing of the 75-80° (at 7 mm) fraction gave a small amount of C_2Cl_6, m.p. 186°.

Photodecomposition reaction of β-chloroethyltriethylsilane. A mixture of the α- and β-isomers of chloroethyltriethylsilane, fraction 69-83° (9 mm), weight 5 g, hydrolyzable chlorine content 10.2%, was illuminated with UV-light for 160 hours. When distilled a 70-73° (9 mm) fraction was collected; a 80-82° fraction was absent. The hydrolyzable chlorine content in the isolated fraction was 6.68%. The residue in the distillation flask was a resinous mass.

Reaction of $(C_2H_5)_4Si$ with CCl_4 in the presence of acetyl peroxide. A reaction mixture of 19 g of $(C_2H_5)_4Si$, 80 g of CCl_4 and 1.8 g of acetyl peroxide was heated for 15 hours; HCl evolution was observed during the reaction process. The amount of unreacted peroxide after reaction was 0.07 g. The mixture was distilled through a fractionation column and the following fractions were collected: 1) 61-65°, 7 g, n_D^{17} 1.4432, d_{20}^{20} 1.4912, $CHCl_3$; 2) 74-77°, 55.6 g, n_D^{17} 1.4630, CCl_4; 3) 152-153°, $(C_2H_5)_4Si$. The residue was kept in a vacuum for 3 hours to remove hexachloroethane, and then distilled. The following fractions were collected:

1) 69-72° (9 mm), 2.0 g, n_D^{17} 1.4490, d_{20}^{20} 0.9206, α-chloroethyltriethylsilane. Found %: Cl total 18.70, Cl hydrolyzable 1.40; C 52.68; H 10.79. 2) fraction 78-82° (9 mm), 3.5 g, n_D^{17} 1.4542, d_{20}^{20} 0.9218, β-chloroethyltriethylsilane. Found %: Cl total 19.81; Cl hydrolyzable 20.09; C 53.01; H 10.43.

SUMMARY

1. The photoreactions of $(C_2H_5)_4Si$, $(C_6H_5)_4Si$ and $CH_3Si(C_6H_5)_3$ with CCl_4 were studied. The last two compounds fail to react with CCl_4. α-Chloroethyltriethylsilane is formed in the reaction of $(C_2H_5)_4Si$ with CCl_4.

2. The reaction of CCl_4 with $(C_2H_5)_4Si$, initiated by acetyl peroxide, gives a mixture of the α- and β-isomers of chloroethyltriethylsilane. Benzoyl peroxide fails to initiate reaction between CCl_4 and $(C_2H_5)_4Si$.

3. The exposure of β-chloroethyltriethylsilane to UV-illumination results in decomposition with the evolution of HCl and the formation of resinous products.

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REACTIONS OF UNSYMMETRICAL ACYL PEROXIDES WITH MERCURY

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It is known that acyl peroxides decompose at the O–O bond, giving free radicals: $(RCO_2)_2 \rightarrow 2RCOO\cdot$, which can then decompose into $R\cdot + CO_2$ (depending on the structure of the R· radical and the reaction conditions used). Both the R· and RCOO· radicals show fixation on a mercury surface to give either mercurous salts or mixed organometallic compounds [1]. It seemed of interest to us to check on the possibility of using reactions of this type to elucidate the relative stability shown by two different acyl radicals.

For this we made a study of the reactions of unsymmetrical acyl peroxides with metallic mercury. We took peroxides of the type $RCO-O-O-CO-C_6H_5$, where R· is either methyl or a phenyl radical with the electron-acceptor NO_2 group as a substitutent in either the meta- or para-position (acetyl benzoyl peroxide, benzoyl p-nitrobenzoyl peroxide and benzoyl m-nitrobenzoyl peroxide). The presence of the benzoyloxy radical in each of the reacting peroxides permitted making a comparison of the other radicals (acetoxy, m- and p-nitrobenzoyloxy) with the benzoyloxy radical and with each other. We selected benzene as the solvent, since it is most inert to the action of radicals in the presence of mercury. The reaction of acetyl benzoyl peroxide with mercury in benzene was run with and without heating. At room temperature the peroxide reacted without CO_2 evolution. The acetoxy and benzoyloxy radicals showed fixation on the mercury to yield mercurous salts of acetic and benzoic acid, respectively. And only by its characteristic odor could the presence of extremely small amounts of methylmercury derivatives be detected. The heating of these components gave CO_2, $(C_6H_5CO_2)_2Hg_2$, $(CH_3CO_2)_2Hg_2$, CH_3HgX and C_6H_5HgX, where X is either the acetic acid or benzoic acid radical. We failed to show the presence of appreciable amounts of either diphenyl or of benzoates. This indicates absence of reaction with the solvent and the initiated character of peroxide decomposition.

The unsymmetrical organomercury compounds RHgOCOR' that we obtained were converted into the corresponding chlorides by exchange reaction with NaCl; here the acyloxy radicals gave sodium acetate and benzoate. At the same time the mercurous salts were converted into calomel and sodium salts. As a result, the acetoxy and benzoyloxy radicals that failed to decompose were determined as the corresponding acids. Our results are summarized in the table. The comparative stability shown by the RCOO· radicals could be judged by the amount of methyl and phenyl derivatives of mercury, acetic acid and benzoic acid that was formed.

From the experimental data it can be seen that 36.5% of the acetoxy radicals lost a CO_2 molecule at 80° and here the methyl radical was converted into CH_3HgX. Also, here 50% of the acetoxy radicals were bound directly to mercury. The total balance for the $CH_3COO\cdot$ radical was 86.5%. Under these conditions a part (19.2%) of the benzoyloxy radicals lost CO_2, and the resulting phenyl radical showed combination as C_6H_5HgX. For the most part the benzoyloxy radicals (81%) were determined as benzoic acid. The total balance for the benzoyloxy group was 100%. The relative stability of the $C_6H_5COO\cdot$ and $CH_3COO\cdot$ radicals can be represented as 8/5. The benzoyloxy radical is more stable due to conjugation of its lone electron with the aromatic nucleus.

For the case of heating either benzoyl m-nitrobenzoyl peroxide or benzoyl p-nitrobenzoyl peroxide with mercury the yield of the organometallic compounds of mercury showed a sharp reduction, in which connection the complete absence of either m- or $p\text{-}O_2NC_6H_4HgX$ was observed. In the experiment using benzoyl m-nitrobenzoyl peroxide the isolated yield of C_6H_5HgX was 11.8%, and 3.9% C_6H_5HgX for benzoyl p-nitrobenzoyl peroxide. As a result, here the formation of the organomercury compounds was exclusively due to decarboxylation of the benzoyloxy radicals. The main reaction products were mercurous salts. Benzoic acid and appreciable amounts of nitrobenzoic acids were isolated in the exchange reactions with $CaCl_2$. Diphenyl and the free nitrobenzoic acids were also found in the reaction products, the formation of which indicates that here the peroxide shows some reaction with the solvent–benzene.

The increased stability shown by the m- and p-$O_2NC_6H_4CO_2\cdot$ radicals can be explained by the fact that the nitro group reduces the electron density of the benzene ring and in this manner augments the conjugation effect shown by the carboxyl group with the ring. The stability shown by the RCOO· radicals that we synthesized in this study increases in the following order:

$$CH_3COO\cdot < C_6H_5COO\cdot < O_2NC_6H_4COO\cdot,$$

which coincides with a similar relationship prevailing for the thermal reactions of unsymmetrical acyl peroxides with benzene [2].

EXPERIMENTAL

Syntheses of unsymmetrical acyl peroxides. Acetyl benzoyl peroxide was obtained from benzaldehyde and acetic anhydride by the method proposed by Nef [3]. Benzoyl m-nitrobenzoyl peroxide and benzoyl p-nitrobenzoyl peroxide were obtained by the respective reaction of the acid chlorides of m-and p-nitrobenzoic acid with sodium perbenzoate.

To 70 ml of an aqueous sodium perbenzoate solution having a concentration of 0.01 g/ml (calculated as perbenzoic acid) was added dropwise 0.8 g of the nitrobenzoyl chloride in 5 ml of anhydrous acetone under cooling and constant stirring. The peroxide precipitate was filtered, washed with water and aqueous acetone, and then air-dried. Weight 0.8-0.9 g (60-70%). The activity of the peroxides was determined by iodometric titration and was 93-95%.

Reaction of acetyl benzoyl peroxide with mercury without heating. A solution of 5 g of acetyl benzoyl peroxide (94.5%) in 50 ml of benzene was shaken with 50 g of metallic mercury at room temperature for 40 hours. The peroxide showed complete reaction in this time. CO_2 evolution was not observed; here mercurous salts were formed as a white powder insoluble in water. After removal of mercury the salts were decomposed by heating with concd. HCl for 3-4 hours. Ether extraction of the solution gave 3.13 g of C_6H_5COOH; after distillation, m.p. 122°. The mixed melting point failed to be depressed. It was shown that acetic acid is present in the aqueous solution. The odor of methyl derivatives of mercury was detected; however, we were unable to isolate them.

Reaction of acetyl benzoyl peroxide with mercury under heating. A solution of 5.0 g of acetyl benzoyl (93.5%) in 50 ml of benzene was shaken with 50 g of mercury under simultaneous benzene boil for 4.5 hours. After this the test for peroxide was negative. The amount of CO_2 collected during the reaction was 0.88 g and methane was not found. After removal of metallic mercury and the addition of 10 g of NaCl the benzene portion and insoluble white precipitate were subjected to steam distillation. The distillate, composed of a benzene and water portion, was separated. Neither diphenyl nor methyl benzoate was found in the benzene portion. From the aqueous portion was isolated 0.25 g of methylmercury chloride with m.p. 173°, and the addition of KI to the filtrate gave 0.7 g of methylmercury iodide.

The mass remaining after steam distillation was filtered and dried, after which it was repeatedly extracted with hot acetone. As a result we obtained 1.6 g (13.8%) of phenylmercury chloride with m.p. 249°. The mixed melting point with authentic phenylmercury chloride was 250°. The mass (6.2 g, 51%) remaining after removal of the phenylmercury chloride was calomel. The addition of KI to the filtrate gave a precipitate of methylmercury iodide (2.2 g). As a result, the total weight of this compound was 2.9 g (31.3%), m.p. 143-144°. The mixed melting point with authentic methylmercury iodide was not depressed. After removal of the methylmercury iodide the solution was acidified with sulfuric acid; here a precipitate of benzoic acid was obtained, which was filtered. The filtrate was steam distilled. The acid distillate was titrated, after which a second acidification gave benzoic acid (2.56 g) with m.p. 121° (from water). The amount of acetic acid was determined from the difference between the total acidity of the distillate and the amount of isolated benzoic acid, being 0.013 mole, and shown to be present by qualitative reactions.

Reaction of benzoyl p-nitrobenzoyl peroxide with mercury.* A solution of 3.0 g of benzoyl p-nitrobenzoyl peroxide (activity 95%) in 50 ml of benzene was heated under stirring with excess mercury for 11 hours. The test for peroxide was negative at the end. On conclusion of reaction the mass was decanted from the mercury, and the latter was washed several times with hot benzene. After distilling off the benzene on the water bath the residue was treated with an excess of saturated $CaCl_2$ solution and then steam distilled. The residue from the steam distillation was filtered and washed with hot water and acetone. The yield of extracted phenylmercury chloride was 0.12 g (3.9%), m.p. 247°. Its mixed melting point with known pure phenylmercury chloride was 249°. The acetone-insoluble portion (2.4 g) represented calomel. The water filtrate contained 0.07 g of free p-nitrobenzoic acid and 1.6 g. of p-nitrobenzoic acid salt. M.p. 232° (from water). The mixed melting point with pure p-nitrobenzoic acid was not depressed. The benzene portion of the distillate gave 0.25 g of diphenyl with m.p. 68-69° (from alcohol). The water portion of the distillate contained 0.09 g of benzoic acid with m.p. 118°. Its mixed melting point with pure benzoic acid was 120°.

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* V. M. Zhulin participated in the experimental part of this and the following experiment.

Reaction of benzoyl m-nitrobenzoyl peroxide with mercury. 3.5 g of benzoyl m-nitrobenzoyl peroxide (activity 93%) in 50 ml of benzene was heated with excess mercury at benzene boil and with stirring for 20 hours. The peroxide showed complete reaction at the end of this time. The reaction mixture was worked up the same as in the preceding. Here we isolated 0.42 g (11.9%) of phenylmercury chloride with m.p. 249°, 0.5 g of m-nitrobenzoic acid with m.p. 135° and 0.09 g of benzoic acid.

SUMMARY

1. The reactions of acetyl benzoyl peroxide, benzoyl m-nitrobenzoyl peroxide and benzoyl p-nitrobenzoyl peroxide with mercury were studied.

2. The stability shown by acyloxy radicals to CO_2-cleavage can be judged from the reaction products (mercurous salts and organometallic compounds).

3. Based on their stability the investigated acyloxy radicals can be arranged in the following order: $O_2NC_6H_4CO_2\cdot > C_0H_5CO_2\cdot > CH_3CO_2\cdot$.

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* T.p. = C. B. Translation pagination.

CONJUGATED SYSTEMS

LXI. THE ADDITION OF ALKYL HALIDES TO DIENE HYDROCARBONS

A. A. Petrov and K. V. Leets

The reaction discovered by A. P. Eltekov [1] for the addition of halide derivates to unsaturated compounds has been subjected to recent detailed study. However, the question of the reaction character of halide derivates with diene hydrocarbons remained untouched.

A good study was made only of the addition of α-chloro ethers to divinyl [2]. It was shown by B. A. Arbuzov and A. N. Pudovik [3] that when divinyl is reacted, for example, with α-chloromethyl ether in the presence of zinc chloride the 1,2-product is obtained, which then under the influence of the same catalyst is isomerized to the 1,4-product. The equilibrium mixture contains about 75% of the latter product. Data also exist on the addition of a series of tetrahalomethanes to divinyl, isoprene, cyclopentadiene and cyclohexadiene under the influence of either peroxides or ultraviolet illumination, in which connection 1,4-addition is predominantly observed [2].

Prior to our investigations only one patent was published on the reaction of divinyl with alkyl halides, in which mention was made of the reactions of divinyl with tertiary butyl chloride and bromide and crotyl chloride and bromide in the presence of either $ZnHlg_2$ or $SnHlg_4$ [4]; here the formation of halide addition products to one, two and more highly combined divinyl molecules was observed, and in the case of unsaturated halides also of their dimers.

We studied the reactions of divinyl, isoprene and diisopropenyl with primary (ethyl bromide), secondary (isopropyl bromide and chloride) and tertiary (tertiary butyl chloride, bromide and iodide) alkyl halides in the presence of either zinc halides or ferric chloride. Preliminary information on the reaction of divinyl with tertiary alkyl halides has already been published [5]. In the future, main attention will be devoted to elucidating the influence shown by the structure of alkyl halides and diene hydrocarbons on the reaction character.

In selecting a catalyst we proceeded from the fact that in the reactions of alkyl halides with ethylene the activity of the catalysts diminishes in the following order [6]: $AlCl_3 > FeCl_3 > BiCl_3 > ZnCl_2$.

The use of $AlCl_3$ promised little success due to its strong polymerizing action on diolefins. The experiments made by us with $FeCl_3$ also gave poor results; consequently we used less active catalysts—the zinc halides—in later experiments. In their presence the reaction usually proceeds with very little heat evolution, which makes it possible to operate with low-boiling hydrocarbons in ordinary apparatus. However, a disadvantage of these catalysts is the fact that reaction is quite slow when halides of low activity are used.

The zinc halides show poor solubility in the starting hydrocarbons and good solubility in the reaction products. This leads to the appearance of an induction period. The addition of a small amount of concentrated hydrogen halide acid to the catalyst results in considerable shortening of the induction period, possibly due to the formation of small amounts of crotyl halides at the expense of the hydrogen halide, which, the same as the reaction products, are capable of dissolving the catalyst. Dissolution of the catalyst, and consequently the start of accelerated reaction, were easily observed by the appearance of a brown color for the mixture.

Increasing the amount of hydrogen halide acid again leads to a reduction in the reaction rate, since here the catalyst shows up in the water phase. However, it is necessary to mention that the addition of acids leads to an increase in the relative yield of secondary polymeric products. To reduce the polymerizing action shown by atmospheric oxygen on diene hydrocarbons we added small amounts of hydroquinone to the mixtures.

The experiments made with primary, secondary and tertiary alkyl halides and divinyl led us to conclude that the nature of the alkyl determines not only the reaction rate, but also its character. The reaction with tertiary alkyl halides proceeds most easily, in which connection only these compounds gave simple low-molecular addition products under our selected reaction conditions. High-boiling oils and tars are obtained in the case of the primary and secondary alkyl halides, from which we were unable to isolate individual substances. The composition of these polymeric products usually corresponds to the formula $R-(C_4H_6)_n-Hlg$, where the average value of n is of the order 6-8.

Together with addition products showing a 1:1 ratio, in the case of the tertiary alkyl halides addition products are formed in which the alkyl halide is added to two, three and more highly combined divinyl molecules (having the general formula given above). With increase of excess alkyl halide the relative yield of low-molecular addition products shows considerable increase (Table 2), in which connection the reaction rate shows simultaneous decrease. To obtain higher yields of the simpler addition products it is necessary to control the reaction course, terminating it at the desired stage and thoroughly removing the catalyst prior to distillation.

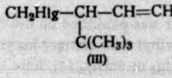
The halogen nature also influences the addition rate of alkyl halides: tertiary butyl bromide shows considerably faster reaction than does tertiary butyl chloride.

Characteristic reaction rate curves (based on change in the vapor pressure of the mixture) for different component ratios are shown in Fig. 1 (Expts. 1, 2 and 3) and Fig. 2 (Expts. 7 and 8).

The structure of the simpler addition products of tertiary alkyl halides with divinyl was shown by their oxidation with either permanganate or ozonization; here tert-butylacetic acid and the corresponding haloacetic acids were isolated in all cases. This information enabled us to select Formula (I) of the three possible for the obtained compounds.

$(CH_3)_3C-CH_2-CH=CH-CH_2Hlg$ (I)

$(CH_3)_3C-CH_2-CHHlg-CH=CH_2$ (II)



$$\underset{\textstyle C(CH_3)_3}{CH_2Hlg-CH-CH=CH_2}$$

(III)

TABLE 1

Substance	Boiling point at 10 mm	d_4^{20}	n_D^{20}	MR	
				found	calc.
$(CH_3)_3C-CH_2-CH=CH-CH_2Cl$	47—47.5°	0.8790	1.4456	44.46	43.54
$(CH_3)_3C-CH_2-CH=CH-CH_2Br$	62—62.5	1.1180	1.4710	47.78	46.44
$(CH_3)_3C-CH_2-CH=CH-CH_2I$	77—79	1.3450	1.5150	53.39	51.48
$(CH_3)_2(C_2H_5)C-CH_2-CH=CH-CH_2Cl$	66—68	0.8960	1.4557	48.72	48.16

In accord with the indicated structure the obtained substances possessed extremely labile halogens. When treated with alcoholic alkali they gave unsaturated ethers: $(CH_3)_3C-CH_2-CH=CH-CH_2OR$.

The constants of the addition products of tertiary butyl halides to divinyl are given in Table 1, and also that of tert-amyl chloride.

It can be seen from the data in Table 1 that for all of the substances the found molecular refraction is somewhat higher than the calculated.

The structure of the addition product of one mole of butyl chloride to two moles of divinyl was also shown by oxidation; here we obtained tert-butylacetic, succinic and chloroacetic acids, on which basis the substance was assigned the formual: $(CH_3)_3C-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2Cl$.

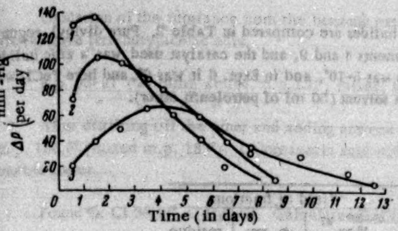


Fig. 1.

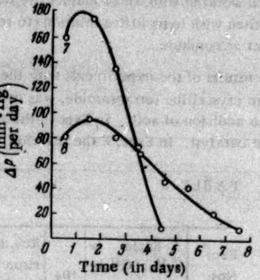


Fig. 2

For the higher addition products we determined only the halogen content, on the basis of which we determined their average empirical formula. These calculations were not exact, since the higher products could contain dimers of the primary addition products.

The fact that only polymeric products are formed as the result of reacting divinyl with primary and secondary alkyl halides is explained by the considerably greater reactivity shown by the primary addition products when compared to the starting halide derivatives. In all cases the reaction shows two kinetics stages. In the first stage the rate of the process is determined by the nature of the starting halide derivative. As a result of this primary reaction a new reagent appears—a halide derivative of the crotyl type. The further course of reaction depends on the addition rate ratio of the starting alkyl halide and the latter substance to divinyl. In the case of the primary and secondary alkyl halides the rate of their addition to divinyl is much slower than is the addition rate of the crotyl type of halide derivative. This leads to the formation of only polymeric forms.

When the tertiary alkyl halides were reacted with isoprene and diisopropenyl we also obtained only polymeric products with average coefficients of n in the formula $R-(C_nH_{2n-2})_n-Hlg$ of the order 2.5-6. These observations are found in agreement with the earlier examined results of the experiments in which divinyl participated. Actually, it is known from the literature that the mobility of the halogen in prenyl chloride (isoprene hydrochloride) is many times its mobility in crotyl chloride. The halogen in diisopropenyl hydrochloride shows even greater mobility [7]. As the result of adding tertiary halide derivatives to isoprene and diisopropenyl there are formed halide derivatives of the prenyl chloride type with extremely high reactivity, which enter into reaction with other molecules of the diene hydrocarbon much more rapidly than to the original halide derivatives.

The presented data agree best of all with the theory of a stepwise ionic mechanism for the addition reaction of halide derivatives to diene hydrocarbons in the presence of zinc halides.

EXPERIMENTAL

Addition of Alkyl Halides to Divinyl

In a thick-walled flask with external cooling (ice + salt) was placed 18 g (0.33 mole) of technical divinyl (C_4H_6 content 90%), 0.25-0.9 mole of alkyl halide, 0.37 mole % of zinc halide (+ 0.1 ml of concentrated hydrogen halide acid) and 0.1 g of hydroquinone. The flask was placed in a thermostat (20°) and hermetically connected through a stopcock with an open mercury manometer, provided with still another stopcock in the closed elbow connected to the flask. The air was evacuated from the system through this last stopcock until repeated evacuation failed to show a pressure drop in the flask. After this the flask was disconnected from the manometer and placed in a mechanical shaker. The pressure in the reaction vessel was measured each day.

The reaction was considered ended when the pressure in the flask failed to drop. Then 50 ml of ether was added to the reaction mixture (to avoid emulsion formation), the ether solution was washed well several times with either water or oxalic acid solution (to remove catalyst), dried over $CaCl_2$ and then distilled, first at atmospheric pressure (to remove most of the starting substances), and then in vacuo. To obtain a better relative yield of the simpler addition products it is necessary to terminate the reaction in the earlier stages.

When working with alkyl iodides the reaction mixture was washed with oxalic acid solution (to remove catalyst), then with hyposulfite solution (to remove iodine), and dried over Na_2SO_4. The distillation was run in an inert gas atmosphere.

The results of the experiments with the tert-butyl halides are compared in Table 2. Pure divinyl, regenerated from crystalline tetrabromide, was used in Experiments 4 and 9, and the catalyst used was a zinc halide without the addition of acid. In Expt. 5 the temperature was 5-10°, and in Expt. 6 it was 0°, and here $FeCl_3$ was used as the catalyst. In Expt. 6 the reaction was run in a solvent (50 ml of petroleum ether).

TABLE 2

Expt. Nos.	Ratio C_4H_6:$(CH_3)_3$-CHlg (in moles)	Hlg	Reaction time (in days)	Total yield (in g)	Yield of fractions			
					45—50° at 10 mm		50—100° at 2.5 mm (in g)	residue (in g)
					(g)	(%)		
1	1 : 0.85	Cl	7	22	8.6	18	5.7	6.8
2	1 : 1.5	Cl	9	27	13.7	28	5.6	6.8
3	1 : 3	Cl	13	26	17.0	35	5.0	3.5
4	1 : 1.5	Cl	17	32.4	21.1	48	3.0	3.1
5	1 : 1.5	Cl	3 (hours)	22	2.2	—	18.5	
6	1 : 1.5	Cl	5 (hours	10	3.6	—	3.7	2.1
7	1 : 1.5	Br	5	42	22.7	36	1.6	17.0
8	1 : 2.5	Br	6	42.	27.0	42	1.6	11.5
9	1 : 1.5	Br	17	32.5	8.5	15	2.0	20.2
10	1 : 1.5	I	8	40	30.1	38	8.0	

Addition of $(CH_3)_3CCl$. Repeated distillation of the fraction with b.p. 45-50° (10 mm) (Table 2) gave a substance (80% of the fraction weight) with the constants given in Table 1.

Found %: Cl 24.15, 23.95. $C_8H_{15}Cl$. Calculated %: Cl 24.18.

The constants of the substances, obtained from pure divinyl (regenerated from the tetrabromide) and from technical divinyl (90% C_4H_6), failed to show a difference.

a) The substance was oxidized with potassium permanganate (10% excess). After reducing the manganese dioxide with SO_2 gas the solution was acidified with H_2SO_4 and then extracted (in an extractor with stirrer), first with benzene, and then ether.

Tert-butylacetic acid was isolated from the benzene fraction.

B.p. 94-96° (26 mm); amide, m.p. 131.5°. Found equiv. 115.4. $C_6H_{12}O_2$. Calculated equiv. 116.2
Literature [8, 9]: b.p. 96° (26 mm); amide, m.p. 132°

The ether extract gave chloroacetic acid. M.p. 56° (from petroleum ether).

Found %: Cl 36.55. Equiv. 94.0. $C_2H_3O_2Cl$. Calculated %: Cl 37.52. Equiv. 94.5.

b) When 4.52 g of the substance was boiled with 20 ml of a 10% KOH solution in methanol for 1 hour 98% of the halogen went into solution. Steam distillation of the reaction mixture gave an unsaturated ether.

B.p. 42-43° (10 mm), n^{20}_D 1.4242. Found %: OCH_3 21.30. $C_8H_{15}OCH_3$. Calculated %: OCH_3 21.82.

A substance (60% of the fraction weight) was isolated from the 2nd fraction (50-100° at 2.5-3 mm).

B.p. 68-73° (2.5 mm), d_4^{20} 0.8874, n_D^{20} 1.4643, MR 62.46. $C_{12}H_{21}Cl\overline{|=}_2$. Calc. 61.55. Found %: Cl 17.82. $C_{12}H_{21}Cl$. Calculated %: Cl 17.66.

Oxidation of the substance from the benzene extract with permanganate (under the conditions described above) gave tert-butylacetic acid.

B.p. 93-97° (26 mm); amide, m.p. 131°; mixed, m.p. 131.5°.

After distilling off the ether and adding acetone to the residue the ether extract gave succinic acid with m.p. 186.5° (mixed m.p. 187°). Chloroacetic acid with m.p. 61° (from petroleum ether) was isolated from the mother liquor.

Found %: Cl 36.92. $C_2H_3O_2Cl$. Calculated %: Cl 37.52.

When the starting substance was treated with 0.5N alcoholic alkali solution on the boiling water bath for 1 hour 92% of the chlorine went into solution.

Distillation of the residue (b.p. above 100° at 2.5 mm) gave the fraction:

B.p. 110-122° (2.5 mm), d_4^{20} 0.9098, n_D^{20} 1.4796, MR 79.51. $C_{16}H_{27}Cl\overline{|=}_3$ Calc. 79.55. Found %: Cl 13.28. $C_{16}H_{27}Cl$. Calculated %: Cl 13.91.

When this fraction was treated with 0.5N KOH 86% of the chlorine went into solution.

The viscous oily residue from the last distillation, failing to distill up to 150° (2.5 mm), had d_4^{20} 0.9422, n_D^{20} 1.4950 and contained 8.31% chlorine, which corresponds approximately to the formula $C_4H_9-(C_4H_6)_6-Cl$.

Addition $(CH_3)_3CBr$. Repeated distillation of the main fraction (48-52° at 5 mm, Table 2) gave a product with the constants shown in Table 1 (84% of the fraction weight).

Found %: Br 41.65, 41.60. $C_8H_{15}Br$. Calculated %: Br 41.82.

a) The ozonization of 5 g of the substance gave 6.2 g of ozonides, which corresponds to 96% ozone absorption. From the benzene extract after decomposing the ozonides was isolated tert-butylacetic acid with b.p. 94-97° (26 mm); amide, m.p. 131.5°; mixed m.p. 131.5°. Bromoacetic acid with m.p. 48° (from petroleum ether) was obtained from the ether extract.

Found %: Br 56.93. $C_2H_3O_2Br$. Calculated %: Br 57.51.

b) Treatment of the substance with alcoholic KOH solution gave an unsaturated ether with b.p. 54.5-55° (10 mm), n_D^{20} 1.4260. Here 96% of the bromine went into solution.

Found %: OC_2H_5 28.93. $C_8H_{15}OC_2H_5$. Calculated %: OC_2H_5 28.84.

Addition of $(CH_3)_3CI$. Repeated distillation of the main fraction (Table 2) gave a substance (83% of the fraction weight) with the constants shown in Table 1.

Found %: I 53.03. $C_8H_{15}I$. Calculated %: I 53.30.

Oxidation of the substance with permanganate gave tert-butylacetic acid (b.p. 94-97° at 26 mm; amide, m.p. 131.5°; mixed m.p. 131.5°).

Found equiv. 116.3. $C_6H_{12}O_2$. Calculated equiv. 116.2.

Treatment of the substance with KOH in methanol gave an unsaturated ether.

B.p. 42-42.5° (10 mm), d_4^{20} 0.7970, n_D^{20} 1.4234, MR 45.48. $C_9H_{18}O|\overline{=}$. Calc. 44.94. Found %: OCH_3 21.44. $C_8H_{15}OCH_3$. Calculated %: OCH_3 21.82.

In this connection 98% of the halogen went into solution.

Addition of $(CH_3)_2(C_2H_5)CCl$. From 19 g (0.32 mole) of divinyl, 50 g (0.48 mole) of $(CH_3)_2(C_2H_5)CCl$ in the presence of 0.6 g of $ZnCl_2$, 0.1 g of concd. HCl and 0.1 g of hydroquinone was obtained 29 g of addition products. The reaction was run for 15 days. Distillation of the substance gave the following fractions: 1) 65-75° (10 mm), 9.2 g; 2) 75-110° (2 mm), 6.2 g; and residue, 12.7 g.

1) A substance with the constants shown in Table 1 was isolated from the 1st fraction.

Found %: Cl 21.93. $C_9H_{17}Cl$. Calculated %: Cl 22.07.

From 5 g of substance was obtained 6.3 g of ozonides, which corresponds to 93.5% ozone absorption. After decomposing the ozonides with water and oxidizing the aldehydes with permanganate at 0° the ozonization products were extracted first with benzene, and then with ether. From the benzene extract was isolated the 3,3-dimethylpentene acid with b.p. 207-213° (755 mm). Its sodium salt was analyzed (recrystallized from acetone).

Found %: C 54.82; H 8.63; Na 15.76. $C_7H_{13}O_2Na$. Calculated %: C 55.25; H 8.61; Na 15.11.

From the ether extract was isolated chloroacetic acid with m.p. 60° (from petroleum ether).

Found %: Cl 37.33. Equiv. 94.90. $C_2H_3O_2Cl$. Calculated %: Cl 37.56. Equiv. 94.50. Literature for the 3,3-dimethylpentene acid [10]: m.p. 209-210°.

When heated with alcoholic alkali for 1 hour the investigated substance lost 93.5% halogen.

2) The following substance was isolated from the 2nd fraction:

B.p. 90-95° (2.5 mm), d_4^{20} 0.9057, n_D^{20} 1.4706, MR 66.23. $C_{13}H_{23}Cl|\overline{=}_2$. Calc. 66.17. Found %: Cl 16.61. $C_{13}H_{23}Cl$. Calculated %: Cl 16.51.

When heated with alcoholic KOH the investigated substance lost 95% of its halogen in 1 hour.

Addition of $(CH_3)_2CHBr$, $(CH_3)_2CHI$ and C_2H_5Br. The results of these experiments are summarized in Table 3.

TABLE 3

Expt. Nos.	Ratio C_4H_6 : RHlg (in moles)	RHlg	Reaction time (in days)	Total yield of product (in g)	Amount of halogen (in %)	n in formula $R-(C_4H_6)_n-Hlg$
1	1 : 3.7	$(CH_3)_2CHBr$	68	6.3	14.27	8.1
2	1 : 4	$(CH_3)_2CHI$	70	5.8	20.54	8.3
3	1 : 4	C_2H_5Br	60	13.3	18.72	5.9

Addition of $(CH_3)_3CCl$ and $(CH_3)_3CBr$ to Isoprene

From 34 g (0.5 mole) of isoprene, 67 g (0.72 mole) of $(CH_3)_3CCl$, 0.5 g of $ZnCl_2$ and 0.1 g of hydroquinone was obtained 42.5 g of oil. The reaction time was four days. The oil failed to distill up to 100° (2 mm).

Found Cl 14.34%, M 492, which corresponds to the formula $[C_4H_9-(C_5H_8)_{2.3}-Cl]_{1.9}$.

For the product obtained under similar conditions from tert-butyl bromide was found the general formula $[C_4H_9{-}(C_5H_8)_{2.5}{-}Br]_{2.3}$.

Addition of $(CH_3)_3CCl$ and $(CH_3)_3CBr$ to Diisopropenyl

From 16.5 g (0.2 mole) of diisopropenyl and 28 g (0.3 mole) of $(CH_3)_3CCl$ was obtained (20 days) 19 g of oil, the greater portion of which (17.9 g) failed to distill up to 150° (2 mm). In this case the end of reaction was determined by the disappearance of reaction with permanganate of the first drops that came over when a test specimen of the substance was steam distilled.

For the residue was found: % Cl 6.89, M (cryoscopically) 650, which corresponds to the average composition $[C_4H_9{-}(C_6H_{10})_{5.2}{-}Cl]_{1.2}$.

In the case of $(CH_3)_3CBr$ under the same conditions a product of average composition $[C_4H_9{-}(C_6H_{10})_{6.1}{-}Br]_{1.3}$, is obtained.

SUMMARY

1. The reaction of divinyl, isoprene and diisopropenyl with primary, secondary and tertiary halide derivatives (selectively) in the presence of zinc halides was studied.

2. It was shown that the reaction is both complex and stepwise in character; here addition products are formed with the general formula $R{-}(C_nH_{2n-2})_n{-}Hlg$.

3. It was established that the reaction rate rises from the primary alkyl halides to the secondary and tertiary, and from divinyl to isoprene and diisopropenyl.

4. The 1:1 type of alkyl halide addition product to dienes was obtained only in the case of divinyl and the tertiary alkyl halides. Their structure as being 1,4-adducts was established by either oxidation or ozonization, where tert-butylacetic and haloacetic acids were obtained.

5. The rules established here were explained on the basis of postulating a stepwise character for the process of adding alkyl halides to dienes, with due consideration for the data given in the literature on the reactivity shown by different types of halide derivatives.

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For the product obtained only [illegible]

[illegible]

Addition of [illegible]

Found % [illegible] of the [illegible]

[illegible] the [illegible] of the substance was [illegible]

For the reaction was found [illegible]

[illegible]

In the case of [illegible] under the same conditions [illegible]

[illegible]

1. The reaction of diallyl, [illegible] in the presence of [illegible]

2. It is shown that the [illegible] formed with the general formula [illegible]

3. It was established that the [illegible]

4. The [illegible] type of allyl halides [illegible] the tertiary allyl halides. [illegible]

5. The [illegible] established here were confirmed [illegible] process of adding [illegible]

LITERATURE CITED

[1] [illegible]

[2] [illegible]

[3] [illegible]

[4] [illegible]

[5] [illegible]

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[8] [illegible]

[9] Dictionary of Organic Compounds [illegible]

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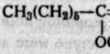
Received June [illegible], 195[illegible]

[illegible] Institute [illegible]

REACTION OF 1-OCTYNE WITH LOWER SATURATED MONOBASIC ACIDS

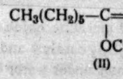
A. I. Bolshukhin and A. G. Egorov

Earlier [1] we described the reaction of phenylacetylene with acetic, propionic and butyric acids, leading to the formation of the corresponding monosubstituted vinyl β-esters and acetophenone. Being interested in the influence of radicals on the addition order of acids to a triple bond and on the properties of the resulting products, we added the same acids in the presence of their mercury salts and boron fluoride etherate to 1-octyne, in which molecule 8 carbon atoms are contained, the same as in phenylacetylene. In all cases we isolated methyl hexyl ketone and the following monosubstituted vinyl esters: 2-acetoxy-1-octene (I), 2-propionyloxy-1-octene (II) and 2-butyroxy-1-octene (III):



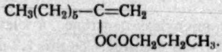
$CH_3(CH_2)_5—C(OCOCH_3)=CH_2$

(I)



$CH_3(CH_2)_5—C(OCOCH_2CH_3)=CH_2$

(II)



$CH_3(CH_2)_5—C(OCOCH_2CH_2CH_3)=CH_2.$

(III)

All of the isolated esters proved to be colorless clear mobile liquids, having a pleasant odor like methyl hexyl ketone. The first of them (I) was described in the literature [2] as being the reaction product of methyl hexyl ketone and ketene itself. Also described in the literature is 1-acetoxy-1-octene, isomeric with the ester (I) obtained by us. It was synthesized by reacting the octanal with acetic anhydride [3].

Only in the synthesis of 2-propionyloxy-1-octene did we find unreacted starting hydrocarbon in the first fraction. With the exception of the ester fractions, methylhexyl ketone was found in all of the fractions. Its presence and amount were established by isolating the semicarbazone. In our experiments from 24 to 35% of the starting hydrocarbon was converted into the ketone.

All of the esters obtained by us were hydrolyzed in the presence of semicarbazide acetate, both at room temperature and when heated. In all cases the semicarbazone of methyl hexyl ketone was isolated. In the cold the hydrolysis rate showed considerable decrease in going from the acetate to the butyrate. The fact that only methyl hexyl ketone is formed in the hydrolysis of the esters supports the validity of the Formulas (I), (II) and (III) assigned to them.

EXPERIMENTAL

We synthesized the starting 1-octyne by reacting sodium acetylenide with 1-bromohexane in liquid ammonia [4], in 81% yield.

B.p. 124-127°, d_0^0 0.7647, d_{20}^{20} 0.7492, d_4^{20} 0.7482, n_D^{20} 1.4150, MR_D 36.89; calc. 37.07.

2-Acetoxy-1-octene [2]. A mixture of 2.0 g of mercuric oxide, 35 g of glacial acetic acid and 3.4 g of acetic anhydride was heated until the mercuric oxide dissolved. To the mixture after cooling was added 1.3 ml of catalyst, $BF_3 \cdot O(C_2H_5)_2$ [5] (b.p. 124-126.5°), and with constant cooling and stirring 55 g of 1-octyne (b.p. 123-126°). The reaction was ended in 50 minutes, but stirring at room temperature was continued another 1.5 hours, after which the reaction mixture was diluted with ether, washed with water, then with soda solution, and dried over calcium chloride. Removal of the solvent gave 70 g of crude product, from which pure 2-acetoxy-1-octene was isolated by 3-fold vacuum distillation. Yield 18 g (21.2%).

B.p. 61.5-62.5° (2 mm), d_0^0 0.9012, d_{20}^{20} 0.8845, d_4^{20} 0.8832, n_D^{20} 1.4270, MR_D 49.49; calc. 49.57.
Found %: C 70.41, 70.47; H 10.69, 10.76. M 164. $C_{10}H_{18}O_2$. Calculated %: C 70.55; H 10.66. M 170.

Here 15-16 g of high-molecular substances were obtained as secondary reaction products, which were not studied, and the presence of 28 g of methyl hexyl ketone was established via its semicarbazone. We failed to show the presence of the starting hydrocarbon in the reaction mixture.

The semicarbazones, isolated from the first and intermediate fractions, all melted at 123-124° (from alcohol) and failed to depress the melting point when mixed with an equal amount of authentic methyl hexyl ketone semicarbazone.

Reaction of 2-acetoxy-1-octene with semicarbazide acetate. A mixture of 3.2 g of semicarbazide hydrochloride, the same amount of potassium acetate and 7-8 ml of water was heated until the salts dissolved completely. After adding 15-17 ml of alcohol and cooling, the liquid phase was separated from the potassium chloride precipitate and added to 1.00-1.05 g of 2-acetoxy-1-octene (b.p. 61.5-62.5° at 2 mm) in a small ground-glass stoppered flask. After good shaking the reaction mixture was either allowed to stand at room temperature for a week or kept in a thermostat at 50-90° for 2-3 hours. In either case the semicarbazone precipitate was filtered, washed with distilled water, and air-dried. For the specimens, allowed to stand for a week at room temperature, the ester showed approximately 70% hydrolysis, while for the specimens that were kept in the thermostat the hydrolysis was quantitative. In both cases the isolated semicarbazones after recrystallization melted at 123-124° (from alcohol). They all failed to depress the melting point when mixed with an equal amount of authentic methyl hexyl ketone semicarbazone.

The hydrolysis of 2-acetoxy-1-octene yields the ketone, and not its isomeric aldehyde.

2-Propionyloxy-1-octene. A solution of 1.7 g of mercuric oxide in 37 g of propionic acid (b.p. 139-141°, n_D^{20} 1.3860) was prepared. To this 1.2 ml of $BF_3 \cdot O(C_2H_5)_2$ catalyst and 55 g of 1-octyne were added at room temperature. The reaction mixture was stirred for 3 hours under water cooling, then diluted with ether, washed with water, then with soda solution until the wash waters showed alkaline, and dried over calcium chloride. Removal of the solvent gave 79.5 g of reaction products, from which as the result of 3-fold vacuum distillation was isolated 2.3 g (2.5%) of pure 2-propionyloxy-1-octene.

B.p. 73-75° (4 mm), d_0^0 0.8965, d_{20}^{20} 0.8817, d_4^{20} 0.8809, n_D^{20} 1.4290, MR_D 53.96; calc. 54.07.
Found %: C 71.72, 71.72; H 10.97, 10.99. M 179, 182. $C_{11}H_{20}O_2$. Calculated %: C 71.69; H 10.94. M 184.

A study of the first and intermediate fractions revealed that 9.0 g of the starting hydrocarbon failed to react, 24 g proved to be combined as high-molecular products, and 18-19 g went for the formation of methyl hexyl ketone, which was established to be present in an amount of 22-23 g via isolation of the semicarbazone.

Reaction of 2-propionyloxy-1-octene with semicarbazide acetate. A weighed sample of 1.00-1.05 g of 2-propionyloxy-1-octene (b.p. 73-75° at 4 mm) was placed in a small ground-glass stoppered flask and covered with 22-23 ml of semicarbazide acetate, prepared the same as described for 2-acetoxy-1-octene. The reaction mixture after shaking was either allowed to stand at room temperature for a week or kept in a thermostat at 50-90° for 2-3 hours. In both cases the semicarbazone of methyl hexyl ketone with m.p. 123-124° was isolated. At room temperature its yield was 47-50% of theory, and when heated in the thermostat it was quantitative. The semicarbazone of the aldehyde isomeric with the ketone was not found.

2-Butyroxy-1-octene. A solution of 1.7 g of mercuric oxide in 44 g of butyric acid (b.p. 161-163°) was prepared. To this was added 1 ml of $BF_3 \cdot O(C_2H_5)_2$ catalyst and in the course of 5-10 minutes 55 g of 1-octyne (b.p. 123-126°). The reaction mixture was stirred for 3 hours and, as needed, cooled with ice water. On conclusion of reaction the products were diluted with ether, washed with soda solution, and dried over calcium chloride.

Removal of the solvent gave 92.2 g of crude product, which after 3 distillations in vacuo gave 40.6 g (41%) of pure 2-butyroxy-1-octene.

B.p. 100.5-101.5° (5 mm), d_0^0 0.8911, d_{20}^{20} 0.8759, d_4^{20} 0.8744, n_D^{20} 1.4318, MR_D 58.80; calc. 58.80.
Found %: C 72.46, 72.67; H 11.06, 11.25. M 191, 194. $C_{12}H_{22}O_2$. Calculated %: C 72.68; H 11.19. M 198.

In this case ester-formation was the main direction of the reaction. Isolation of the semicarbazone from the first and intermediate fractions established the presence of 15.3 g of methyl hexyl ketone. We failed to find any unreacted hydrocarbon.

Reaction of 2-butyroxy-1-octene with semicarbazide acetate. A weighed sample of 1.00-1.05 g of 2-butyroxy-1-octene (b.p. 100-100.5° at 5 mm) was treated with semicarbazide acetate, both at room temperature and at 50-90°, in exactly the same manner as for the preceding esters. In both cases the same methyl hexyl ketone semicarbazone with m.p. 123-124° was isolated, failing to depress the melting point when mixed with an equal amount of the authentic product.

The yield of semicarbazone, formed at room temperature, was 9-10%, and when heated it was quantitative. The semicarbazone of the octanal was not found.

SUMMARY

1. Three monosubstituted vinyl esters were described: 2-acetoxy-1-octene, 2-propionyloxy-1-octene and 2-butyroxy-1-octene, the last two for the first time.

2. The method used to find the position of the acyloxy group in the ester molecules was to hydrolyze the latter in the presence of semicarbazide acetate, both at room temperature and under heating.

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* T.p. = C. B. Translation pagination.

In this case, error [illegible] any unreacted [illegible].

Deviation of [illegible]

The yield of [illegible]

[illegible]

1. [illegible]

2. [illegible] presence of [illegible]

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(1) A. A. Robertson and [illegible]

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Received March [illegible]

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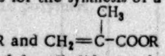
THE SYNTHESIS OF ALKYLIDENE AND ARYLIDENE GLYCOL ESTERS OF ACRYLIC AND METHACRYLIC ACIDS

I. A. Arbuzova, S. A. Plotkina and V. N. Efremova

Acrylic and methacrylic acid derviatives are assuming constantly greater importance in connection with the technically valuable properties of their polymers: unsurpassed clarity, lack of color, stability to the action of light and heat, etc.

Methods for the synthesis of a large number of acrylic and methacrylic acid esters of general formula $CH_2{=}CHCOOR$ and  $CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}COOR$ are indicated in the literature [1, 2]; however, there is hardly any data on the synthesis of the alkylidene and arylidene glycol esters. According to patent statements, of the alkylidene glycol esters the ethylidene glycol dimethacrylate was obtained together with the vinyl ester of methacrylic acid by the additionof acetylene to methyacrylic acid in the presence of mercuric sulfate as catalyst.

The usual method of preparing esters of acetic acid–ethylidene diacetate, benzylidene diacetate, allylidene diacetate, etc.–consists in reacting acetic anhydride with aldehydes in the presence of a catalyst (sulfuric acid). We established that this method can also be extended to the anhydrides of unsaturated acids. When aldehydes were reacted with acrylic and methacrylic anhydrides in the presence of inhibitors (to prevent polymerization) we obtained the lidene glycol esters in 35 to 55% yield.[*] The obtained esters are clear colorless liquids, readily polymerizing in the sunlight at room temperature, and also in the presence of peroxides, into infusible colorless glassy products, insoluble in organic solvents. The properties of our synthesized products are given in Table 1.

EXPERIMENTAL

Preparation of Starting Products

Acrylic anhydride. To 85 g of acrylic acid with b.p. 48-50° (10 mm), 0.3 g of 85% phosphoric acid (catalyst) and 0.1 g of copper powder (inhibitor) was added 90 g of acetic anhydride in two portions. The mixture was heated in an oil bath. The acetic acid formed in the reaction was distilled through a Vigreux column (70 cm high), connected to the reaction flask. The residue was vacuum distilled. The yield of acrylic anhydride with b.p. 55-56° (6 mm) was 51 g (68.6%).

Methacrylic anhydride. To 120 g of methacrylic acid with b.p. 55-56° (5 mm), 0.5 g of phosphoric acid and 1 g of copper powder was added 102 g of acetic anhydride in two portions. After distilling off the acetic acid the residue was distilled under reduced pressure. The yield of methacrylic anhydride with b.p. 76-77° (8 mm) was 63.5 g (59.1%).

Synthesis of Alkylidene Glycol Esters

Ethylidene glycol diacrylate. To 12.6 g of freshly distilled acrylic anhydride in a round-bottomed flask, fitted with stirrer, condenser and dropping funnel and cooled with ice water, wereadded 0.08 ml of sulfuric acid (93%) and 0.1 g of cuprous chloride (inhibitor). To the mixture was gradually added with stirring 6.9 g of freshly distilled acetaldehyde. The mixture was let stand at room temperature for 24 hours, after which the sulfuric acid was neutralized with sodium acetate, while the reaction product was distilled under reduced pressure in the presence of picric acid (inhibitor). From the distillation was isolated 9.28 g (54.6%) of ethylidene glycol diacrylate with b.p. 61-65° (4 mm). When distilled a second time the substance boiled at 61-62° (4 mm).

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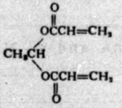
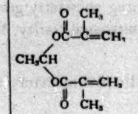
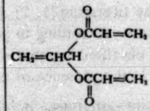
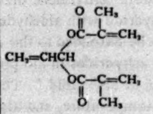
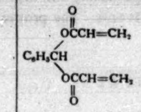
[*] The actual yields are considerably higher. Despite the use of inhibitors, purification of the esters by distillation under reduced pressure results in large losses due to polymerization in the distillation flask.

TABLE 1

Properties of Monomeric Alkylidene and Arylidene Glycol Esters.

Expt. Nos.	Name	Formula	Boiling point at pressure (mm)	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.
1	Ethylidene glycol diacrylate	 $CH_3CH(OCOCH{=}CH_2)_2$	61—62°(4)	1.0508	1.4243	41.46	41.52
2	Ethylidene glycol dimethacrylate	 $CH_3CH(OCOC(CH_3){=}CH_2)_2$	74 (6)	1.0277	1.4370	50.5	50.75
3	Allylidene glycol diacrylate	 $CH_2{=}CHCH(OCOCH{=}CH_2)_2$	71—72 (5)	1.0598	1.4390	45.19	45.67
4	Allylidene glycol dimethacrylate	 $CH_2{=}CHCH(OCOC(CH_3){=}CH_2)_2$	98—99 (6)	1.0420	1.4567	54.88	54.90
5	Benzylidene glycol diacrylate	 $C_6H_5CH(OCOCH{=}CH_2)_2$	114 (4)	1.1170	1.4945	60.54	61.00

Found saponification number: 672. $C_8H_{10}O_4$. Calculated saponification number: 671.9.

Ethylidene glycol dimethacrylate. To a mixture of 30.8 g of methacrylic anhydride, 0.03 ml of sulfuric acid (93%) and 0.1 g of cuprous chloride was added dropwise 8.8 g of acetaldehyde. Then the reaction mixture was heated on the water bath at 40-45° for 50 minutes and allowed to stand at room temperature for 18 hours. Then the mixture was diluted with ether and washed with water. After drying over calcium chloride the ether was removed, while the residue was distilled under reduced pressure in the presence of picric acid (inhibitor). The yield of ethylidene glycol dimethacrylate with b.p. 72-74° (5 mm) was 9.5 g (24.6%).

Found %: C 60.20; H 7.40. $C_{10}H_{14}O_4$. Calculated %: C 60.50; H 7.12.

The heating of ethylidene glycol methacrylate with 0.3% benzoyl peroxide gave a hard, colorless, transparent glassy polymer.

Allylidene glycol diacrylate. To 25.2 g of acrylic anhydride, 0.2 ml of sulfuric acid (98%) and 0.3 g of cuprous chloride, cooled in an ice-salt bath, was added 11.2 g of freshly distilled acrolein, after which the mixture was stirred at room temperature for 3 hours, and then let stand for 17 hours. The sulfuric acid was neutralized with sodium acetate, while the reaction product was distilled under reduced pressure. The yield of allylidene glycol diacrylate with b.p. 71.5-74.5° (8 mm) was 13.9 g (38.1%). After a second distillation the substance had b.p. 71-72° (5 mm).

On standing the substance polymerized into a hard, colorless glassy polymer.

Allylidene glycol dimethacrylate. To 17 g of methacrylic anhydride and 0.02 ml of sulfuric acid (98%) was added 7.8 g of freshly distilled acrolein, after which the mixture was heated for 2 hours at 50°, and after cooling was distilled under reduced pressure in the presence of benzidine (inhibitor). The yield of allylidene glycol dimethacrylate with b.p. 98-99° (6 mm) was 6.8 g (29.3%). The residue in the flask polymerized.

Benzylidene glycol diacrylate. To 12.6 g of acrylic anhydride, 10.6 g of freshly distilled benzaldehyde and 0.1 g of copper powder was added 0.025 ml of sulfuric acid (98%). The mixture was allowed to stand for 20 hours and then distilled under reduced pressure (in the presence of picric acid). The yield of benzylidene glycol diacrylate with b.p. 72-74° (5 mm) was 9.65 g (41%). On standing the product polymerized.

SUMMARY

1. The alkylidene and arylidene glycol esters of acrylic and methacrylic acids were synthesized by reacting aldehydes with acrylic and methacrylic anhydrides.

2. The obtained esters are readily polymerized under the influence of light, heat or peroxides to yield glassy trimeric polymers.

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SYNTHESIS OF CHLOROPHENYL ESTERS OF METHACRYLIC ACID

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In contrast to the aliphatic and arylalkyl esters of acrylic and methacrylic acids, comparatively little consideration has been given in the literature to the aryl acrylates and aryl methacrylates [1]. The present communication is devoted to the problem of synthesizing a number of chloro-substituted phenyl esters of methacrylic acid. Statements exist in the literature on a method of preparing the p-chlorophenyl and 2, 4-dichlorophenyl methacrylates, obtained by reacting methacrylyl chloride with an aqueous solution of the corresponding sodium phenolate. When the synthesis was run with the 2,6-di- and 2,4,6-trichlorophenols the indicated method failed to give a positive result [2]. Nencki and Heyden indicate the preparation of substituted phenyl esters of salicylic acid by reacting thionyl chloride with a mixture of the acid and the corresponding phenol [3].

We synthesized the o-chlorophenyl, p-chlorophenyl, 2,4-dichlorophenyl, 2,4,6-trichlorophenyl and pentachlorophenyl esters of methacrylic acid. The synthesis was accomplished by reacting the corresponding chlorophenol with methacrylyl chloride under heating and with removal of the hydrogen chloride formed here, and also in pyridine medium, where the hydrogen chloride was bound. The chloro-substituted phenyl esters of methacrylic acid were also obtained by treating a mixture of the corresponding chlorophenol and methacrylic acid with thionyl chloride.

The monochloro-substituted esters of methacrylic acid are colorless transparent oily liquids with a sharp disagreeable odor; the 2,4-dichloro-, 2,4,6 trichloro- and pentachloro-phenyl methacrylates are crystalline. When heated with benzoyl peroxide the chlorophenyl esters are polymerized into transparent glassy polymers. The properties of the chloro-substituted phenyl esters obtained by us are given in the table.

TABLE

Properties of Chloroaryl Methacrylates $CH_2{=}C(CH_3)\,COOR$

Expt. Nos.	R	Boiling point	Melting point	Physical constants				Analysis for Cl (%)	
				d_4^{20}	n_D^{20}	MR_D		found	calc.
						found	calc.		
1	o-Chlorophenyl. .	98—99° (3 мм)	—	1.1739	1.5268	51.45	50.83	18.15	18.04
2	p-Chlorophenyl. .	113—114 (6 мм)	—	1.1823	1.5292	50.28	50.83	17.73	18.04
3	2,4-Dichlorophenyl	133—133.5 (10 мм)	55—56°	1.249 *	1.5239 *	—	—	30.51	30.70
4	2,4,6-Trichlorophenyl	—	61—61.5	—	—	—	—	40.14	40.08
5	Pentachlorophenyl	—	91—91.5	—	—	—	—	52.91	53.06

* The determinations were run at 56.5°.

EXPERIMENTAL

Methacrylyl chloride. A mixture of 86 g of methacrylic acid with b.p. 65° (11 mm) and 119 g of thionyl chloride was prepared. At first the reaction was run with slight warming, and at the end the reaction mixture was heated at 40° for 3 hours. The yield of methacrylyl chloride with b.p. 98-99° (770 mm) was 78 g (65%); literature [4], b.p. 98.9-99.1° (770 mm).

o-Chlorophenyl methacrylate. To 25.7 g of o-chlorophenol (b.p. 165-166°, 742 mm) in a round-bottomed flask, fitted with a dropping funnel and reflux condenser with calcium chloride tube, and heated to 45°, was gradually added 23 g of methacrylyl chloride. After this the mixture was heated at 70-80° for 2.5 hours, and on conclusion of heating it was distilled under reduced pressure in a nitrogen stream. The yield of o-chlorophenyl methacrylate with b.p. 95-97° (3 mm) was 34.6 g (89%). A second distillation gave 23.03 g (58.6%) of product with b.p. 98-99° (3 mm).

Found %: Cl 18.15. $C_{10}H_9O_2Cl$. Calculated %: Cl 18.04.

The heating of o-chlorophenyl methacrylate in the presence of benzoyl peroxide gave a hard colorless, transparent, glassy polymer.

p-Chlorophenyl methacrylate. a) To 25.7 g of molten p-chlorophenol was gradually added under stirring 22.9 g of methacrylyl chloride. The mixture was let stand at room temperature overnight and the next day was heated at 70° under stirring for about 2.5 hours (until hydrogen chloride ceased to evolve). Then the reaction product was dissolved in ether, washed with 4% aqueous sodium hydroxide solution, then with water, and dried over calcium chloride. After removal of the ether the residue was distilled under reduced pressure. The yield of the p-chlorophenyl ester was 28.9 g (73.5%), b.p. 126-128° (13 mm). After a second distillation in the presence of an inhibitor (cuprous chloride) the b.p. was 93-94° (2 mm), d_4^{20} 1.1791, n_D^{20} 1.5282.

Found %: Cl 18.15. $C_{10}H_9O_2Cl$. Calculated %: Cl 18.04.

b) To a mixture of 192.75 g of p-chlorophenol and 146 g of methacrylic acid was gradually added under stirring 200.9 g of thionyl chloride, after which the reaction was run the same as described in Experiment "a" up through the point of dissolving in ether. Here the mixture was treated with a 10% aqueous soda solution. Removal of the ether by distillation gave 237.1 g (80%) of crude product, which was distilled under reduced pressure in a carbon dioxide stream and in the presence of cuprous chloride. The yield of p-chlorophenyl methacrylate was 156.2 g (53.0%), which when heated in the presence of benzoyl peroxide suffered polymerization into a hard glassy polymer.

2,4-Dichlorophenyl methacrylate. a) To 48.9 g of 2,4-dichlorophenol was gradually added 34.5 g of methacrylyl chloride. After this the reaction mixture was heated at 90-92° for 3 hours. The ester obtained here was distilled from the reaction flask under reduced pressure in the presence of cuprous chloride. The yield of the 2,4-dichlorophenyl ester was 57.2 g (82.7%), b.p. 133-133.5°; m.p. 50-51°. After recrystallization from a mixture of alcohol and benzene the ester had m.p. 55-56°.

b) To a mixture of 81.5 g of 2,4-dichlorophenol and 45 g of methacrylic acid (heated to melting of the dichlorophenol) was gradually added under stirring 54.4 g of thionyl chloride. The reaction mixture was let stand at room temperature for 50 hours and then heated at 70° for about 2 hours (until the evolution of hydrogen chloride ceased). On conclusion of heating the reaction mixture was poured into an aqueous 4% sodium hydroxide solution. The resulting precipitate was filtered, dissolved in ether, and the ether solution was additionally washed with 4% alkali solution and water, after which it was dried. After removal of the ether the crude product was recrystallized from a mixture of alcohol and benzene. The yield of 2,4-dichlorophenyl methacrylate as needle crystals was 89 g (77.0%), m.p. 55.5-56°.

Found %: Cl 30.4. $C_{10}H_8O_2Cl_2$. Calculated %: Cl 30.7.

2,4,6-Trichlorophenyl methacrylate. a) To 67.2 g of 2,4,6-trichlorophenol and 34.4 g of methacrylic acid at 35-40° was gradually 41.8 g of thionyl chloride. Then the reaction mixture was heated at 40-60° for ~10 hours (until hydrogen chloride ceased to evolve). The solid reaction mass was dissolved in ether. Further treatment was the same as in Experiment "b", described for p-chloro phenyl methacrylate. Recrystallization of the crude product from alcohol containing several drops of acetone gave 57.3 g (61.6%) of needle crystals with m.p. 61-61.5°.

b) Forty grams of 2,4,6-trichlorophenol was dissolved in 126.5 g of pyridine. To the solution was gradually added under stirring 23 g of methacrylyl chloride. Then the mixture was heated at 90° for 3 hours. The hot mixture was poured into water made acid with hydrochloric acid. The resulting 2,4,6-trichloro-phenyl methacrylate crystals were filtered, washed with water made acid with hydrochloric acid, and then dissolved in ether and treated with sodium hydroxide solution. Removal of the ether and recrystallization from alcohol gave 39.8 g (74.0%) of substance. A second recrystallization gave crystals with m.p. 61-61.3°.

Found %: Cl 39.61. $C_{10}H_7O_2Cl_3$. Calculated %: Cl 40.08.

Pentachlorophenyl methacrylate. To a mixture of 80 g of pentachlorophenol (m. p. 186-187°) and 73.5 g of pyridine at 70° was gradually added 47 g of methacrylyl chloride. The reaction mixture was heated for 2 hours at 70°. Subsequent treatment was the same as in the preceding synthesis. The yield of pentachlorophenyl methacrylate was 76 g (75.7%). Two recrystallizations from a mixture of alcohol and benzene gave 59.4 g (59.2%) of substance with m.p. 91-91.5°.

Found %: Cl 52.91. $C_{10}H_5O_2Cl_5$. Calculated %: Cl 53.03.

SUMMARY

1. The new o-chlorophenyl, 2,4,6-trichlorophenyl and pentachlorophenyl esters of methacrylic acid were synthesized.

2. The p-chlorophenyl, 2,4-dichlorophenyl and 2,4,6-trichlorophenyl methacrylates were obtained by reacting methacrylyl chloride with the corresponding chlorophenol, and also by treating a mixture of the chlorophenol and methacrylic acid with thionyl chloride.

3. When heated in the presence of benzoyl peroxide the chlorophenyl esters of methacrylic acid suffer polymerization to yield transparent glassy polymers.

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[illegible] only added water [illegible] this hot mixture was poured into [illegible]

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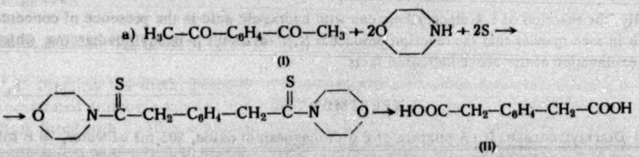
SYNTHESES BASED ON 1,4-DIACETYLBENZENE

A. M. Sladkov and S. V. Vitt

1,4-Diacetylbenzene is an extremely convenient starting substance for the synthesis of diverse p-bifunctional benzene derivatives (dicarboxylic acids, diamines, etc.) the preparation of which is not always easily realized by other methods. The products obtained here represent undoubted interest for the synthesis of high-molecular compounds of either the nylon or terylene type.

The synthesis of 1,4-diacetylbenzene was described by Berend and Herms, who obtained it by hydrolyzing either the terephthalyldiacetic [1] or terephthalyldiacetoacetic [2] ester with 10% sulfuric acid. To obtain 1,4-diacetylbenzene Ingle [3] proceeded from terephthalyldimalonic ester, heating the latter with an alcoholic sulfuric acid solution. Riemschneider [4] obtained 1,4-diacetylbenzene by oxidizing 1,4-diethylbenzene with either potassium or silver permanganate, in which connection the yield of the diketone reached 55%.

In our work we obtained 1,4-diacetylbenzene in 50% yield by the oxidation of 1-ethyl-4-acetylbenzene with neutral potassium permanganate solution. Starting with 1,4-diacetylbenzene (I), we obtained p-phenylenediacetic acid (II), 1',4'-diamino-1,4-diethylbenzene (III), p-xylylenediamine (IV), p-phenylenediamine and some of their derivatives by the following schemes:


a) $H_3C-CO-C_6H_4-CO-CH_3 + 2O$ NH + 2S →
(I)
S
S
→ O N—C—$CH_2-C_6H_4-CH_2$—C—N O → $HOOC-CH_2-C_6H_4-CH_2-COOH$
(II)

b) $(I) + 2HCONH_2 \rightarrow \underset{(III)}{H_3C-CH(NH_2)-C_6H_4-CH(NH_2)-CH_3}$

c) $(II) + 2NaN_3 \xrightarrow{H_2SO_4} \underset{(IV)}{H_2N-CH_2-C_6H_4-CH_2-NH_2} + 2CO_2 + 2N_2$

d) $(I) + 2NaN_3 \xrightarrow{H_2SO_4} \underset{(V)}{H_3C-CO-HN-C_6H_4-NH-CO-CH_3} + 2N_2$

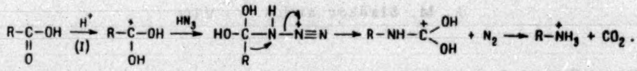
p-Phenylenediacetic acid (II) was obtained earlier from p-xylylene dibromide through the dinitrile [5-8]; Substance (III) was synthesized by reducing the dioxime of 1,4-diacetylbenzene with sodium amalgam in alcohol solution [9], while the synthesis of (IV) was described by Lustig [10], who proceeded from p-xylylene-bis-phthalimide, which was hydrolyzed with a mixture of acetic and sulfuric acids.

Of interest is the fact that when p-phenyenediacetic acid is reacted with hydrazoic acid by the Schmidt reaction it shows simultaneous reaction of both carboxyl groups, whereas in the case of terephthalic acid only one carboxyl group enters into this reaction [11]. We see such a difference in the behavior of homologous acids as being due to the fact that the positive charge, arising at the nitrogen atom as the result of eliminating one carboxyl group from terephthalic acid, prevents progress of reaction for the other carboxyl group:

$$HOOC{-}C_6H_4{-}COOH \xrightarrow{HN_3,\ H_2SO_4} HOOC{-}C_6H_4{-}\overset{+}{N}H_3 \xrightarrow{HN_3,\ H_2SO_4} \text{Reaction fails to go further.}$$

$$\text{(II)} \xrightarrow{HN_3,\ H_2SO_4} HOOC{-}CH_2{-}C_6H_4{-}CH_2{-}\overset{+}{N}H_3 \xrightarrow{HN_3,\ H_2SO_4} \overset{+}{H}N_3{-}CH_2{-}C_6H_4{-}CH_2{-}\overset{+}{N}H_3.$$

In our opinion, the influence of a positively charged center on the progress of the Schmidt reaction consists in a reduction of the electron density at the carbon atom of the carboxyl group, as the result of which the possibility is excluded of forming a stable carbonium ion in accord with Reaction (I):



$$R{-}\underset{\underset{O}{\|}}{C}{-}OH \xrightarrow[(I)]{H^+} R{-}\underset{\underset{OH}{|}}{\overset{+}{C}}{-}OH \xrightarrow{HN_3} HO{-}\underset{\underset{R}{|}}{\overset{\overset{OH}{|}}{C}}{-}\overset{\overset{H}{|}}{N}{-}\overset{+}{N}{\equiv}N \longrightarrow R{-}NH{-}\overset{+}{C}\genfrac{}{}{0pt}{}{OH}{OH} + N_2 \longrightarrow R{-}\overset{+}{N}H_3 + CO_2.$$

On the contrary, in the case of p-phenylenediacetic acid, due to absence of conjugation, the positively charged center that arises here fails to evoke a reduction in the electron density at the carbon atom of the carboxyl group. It could be expected that a nitrogen atom, standing in the para-position to a carboxyl group, in the case where it is deprived of the possibility of transformation into the ammonium state under the reaction conditions, will fail to exert an influence on the ability of the carboxyl group to enter into the Schmidt reaction.

It is evident that in the Schmidt reaction process 1,4-diacetylbenzene (in contrast to terephthalic acid) should form not the ammonium ion of type $Ar{-}\overset{+}{N}H_3$, but instead the amide of structure $Ar'NHCOCH_3$.* Consequently, the acylamido group in p-acetylacetanilide, being an intermediate product in Reaction "d", should not exert a hindering influence on progress of reaction for the second acetyl group:

$$p\text{-}CH_3COC_6H_4COCH_3 \longrightarrow p\text{-}CH_3COC_6H_4{-}NHCOCH_3 \longrightarrow p\text{-}CH_3CONHC_6H_4NHCOCH_3.$$

Actually, the reaction of 1,4-diacetylbenzene with hydrazoic acid in the presence of concentrated sulfuric acid proceeds in such manner that the reaction product is N,N'-diacetyl-p-phenylenediamine, which completely supports the explanation of the above indicated facts.

EXPERIMENTAL

1) 1,4-Diacetylbenzene (I). A mixture of 8 g of magnesium oxide, 205 ml of water, 26.8 ml of nitric acid (d 1.4) and 31.7 g of potassium permanganate was heated on the water bath at 60° until the magnesium oxide and potassium permanganate dissolved completely. Then at the same temperature with vigorous stirring was added 15 g of 1-ethyl-4-acetylbenzene. The stirring at 60° was continued for 4 hours, after which the reaction products were filtered while hot to remove manganese dioxide. The precipitate on the filter was thoroughly washed with hot alcohol (twice with 50 ml portions), and then with benzene (twice with 50 ml portions). The aqueous filtrate was extracted with benzene (twice with 50 ml portions). The benzene extract was added to the alcohol-benzene extract and boiled for 10 minutes with 5 g of activated carbon, after which the carbon was removed by filtration. After distilling off the solvent the residue and unoxidized 1-ethyl-4-acetylbenzene (showing crystallization when cooled) were recrystallized from 70% methanol. The yield of 1,4-diacetylbenzene was 8.2 g (50%), m.p. 113-114°; m.p. 114° [4]. The mixed melting point with a specimen of the pure product failed to be depressed.

Dioxime m.p. 214°; m.p. 213° (by [4]). Found %: N 14.66. $C_{10}H_{12}O_2N_2$. Calculated %: N 14.58.

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* This follow from an examination of the known data on the reactions of acid amides. For example, the facts of facilitated ortho- and para-substitution in either the nitration or sulfonation of acetanilide [12, 13] suggest that the equilibrium for the reaction $ArNHCOCH_3 + H^+ \rightleftharpoons Ar\overset{+}{N}H_2COCH_3$ is shifted to the left in view of the low basicity shown by acid amides.

2) p-Phenylenediacetic acid bisthiomorpholide. A mixture of 8.2 g of (I), 17 g of morpholine and 8 g of sulfur was boiled for 2.5 hours. The crystals, which separated when the reaction mass was cooled, were filtered and washed with alcohol. The yield of thiomorpholide with m.p. 204° was 17.5 g. Recrystallization from dioxane gave 9.8 g (55%) of p-phenylenediacetic acid bisthiomorpholide with m. p. 206-207°, obtained as lemon-yellow leaflets (not described in the literature).

Found %: N 7.78. $C_{18}H_{16}O_2N_2S_2$. Calculated %: N 7.86.

3) p-Phenylenediacetic acid (II). A mixture of 3.25 g of the obtained thiomorpholide and 50 ml of acetic acid was boiled for 5 hours. To the mixture during boiling was added 25 ml of concentrated hydrochloric acid (in portions of 10, 10 and 5 ml). The reaction products were evaporated to a volume of 10 ml, after which 10 ml of water was added to the residue, and the mixture was let stand overnight. The crystals obtained here were filtered, dissolved in 40 ml of 10% potassium carbonate solution, the solution decolorized by heating with activated carbon, the carbon removed by filtration, and the filtrate made acid with hydrochloric acid. The yield of colorless product with m.p. 244° was 2.5 g. The acid was recrystallized from a mixture of benzene and glacial acetic acid. Yield 1.6 g (90%), m.p. 246-247°; literature: m.p. 236 [7], 244° [8].

Found: Neutralization equivalent 96.5. Calculated: 97.0.

The obtained p-phenylenediacetic acid was converted into the dimethyl ester; m.p. 57-58°; literature: 56.5-57° [8].

4) p-Xylylenediamine. A mixture of 2.4 g of p-phenylenediacetic acid, 40 ml of concentrated sulfuric acid and 80 ml of chloroform was treated for 30 minutes at 40-50° with 2.6 g of sodium azide (added in small portions), after which the mixture was let stand for a day. Then the products were poured into water, and the chloroform layer separated and washed with water. An excess of sodium hydroxide was added to the combined aqueous solution, and then 7 g of benzoyl chloride under ice-cooling and stirring. The resulting crystals were filtered, and washed successively with 5% hydrochloric acid, water, 5% sodium hydroxide and again with water. Recrystallization from dioxane gave 3.84 g (90%) of the bibenzoyl derivative (IV) with m.p. 194-195°; literature [10]: m.p. 194°.

Found %: N 9.22. $C_{22}H_{20}O_2N_2$. Calculated: N 9.10.

5) 1',4'-Diamino-1,4-diethylbenzene. To a mixture of 16.2 g of (I) and 50 ml of formamide was added 2 ml of concentrated ammonia solution and 1 ml of formic acid. The mixture was heated for 4 hours at 200-205° in a flask fitted with a reflux condenser, having a wide internal tube (not less than 15 mm to avoid plugging). On conclusion of reaction an excess of concentrated hydrochloric acid was added to the reaction mass, and the mixture was heated for 1.5 hours on the boiling water bath. Then the reaction products were made strongly alkaline and subjected to continuous extraction with benzene for 12 hours. The solvent was removed from the benzene layer by distillation, and the residue was vacuum distilled. The yield of amine with b.p. 128-129° (4 mm) was 10.5 g (65%). From the literature [14]: b.p. 140° (12 mm). From the amine was obtained N,N'-diacetyl-1',4'-diaminodiethylbenzene with m.p. 218°.

Found %: N 11.37. $C_{14}H_{18}O_2N_2$. Calculated: N 11.46.

6) p-Phenylenediamine. To a stirred mixture of 1.62 g of (I), 35 ml of benzene and 24 ml of concentrated sulfuric acid was added 1.95 g of sodium azide at 30-35° (over 15 minutes). The reaction mixture was stirred at 30-35° for 30 minutes, and then for 15 minutes at 45-50°. The reaction mixture after cooling was poured into water. The solid was filtered, washed with water, and recrystallized from acetic acid. The yield of p-phenylenediamine diacetate with m.p. 303-304° [15] was 1.59 g.

Found %: N 14.86. $C_{10}H_{12}O_2N_2$. Calculated %: N 14.57.

SUMMARY

1. Starting from p-diacetylbenzene we synthesized: p-phenylenediacetic acid, 1',4'-diamino-1,4-diethylbenzene, p-xylylenediamine, p-phenylenediamine and some of their derivatives.

2. It was shown that in the Schmidt reaction p-phenylenediacetic acid shows simultaneous reaction of both carboxyl groups, in contrast to terephthalic acid. An explanation of this fact is given.

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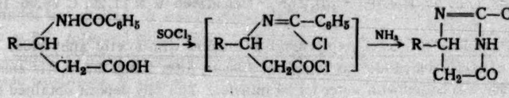
TETRAHYDROPYRIMIDINE COMPOUNDS

III. SYNTHESIS OF SUBSTITUTED 4-PIPERONYL-6-OXOTETRAHYDROPYRIMIDINES

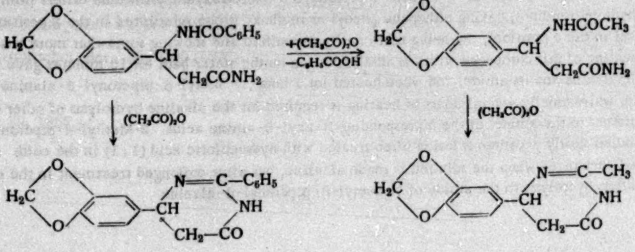
V. M. Rodionov* and V. V. Kiseleva

Earlier [1] we had studied the formation of substituted 6-oxotetrahydropyrimidines from acylated β-phenyl-β-alanines and their amides, and on the whole confirmed the data of V. M. Rodionov and V. K. Zvorykina [2, 3] relative to obtaining 6-oxotetrahydropyrimidines from acetylated β-amino acids of the aliphatic series. To be sure, in our cases the reaction for closure of the tetrahydropyrimidine ring was strongly complicated by the processes of desamination and transacylation.

The purpose of the present study was to verify our conclusions on another member of the aromatic β-amino acids—β-piperonyl-β-alanine. It was revealed that here secondary reactions render formation of the pyrimidine ring even more difficult. Thus, if N-benzoyl-β-pheny-β-alanine is heated with thionyl chloride at 80° ring closure proceeds quite smoothly in accord with the general scheme:



while in the case of N-benzoyl-β-piperonyl-β-alanine closure of the tetrahydropyrimidine ring is completely absent, and only the desamination reaction prevails, leading to the amide of piperonylacrylic acid. The corresponding 4-piperonyl-6-oxotetrahydropyrimidines can be obtained only by treating the amides of N-acyl-β-piperonyl-β-alanines with acetic anhydride, although here also the cyclization reaction is accompanied by secondary processes. For the amide of N-benzoyl-β-piperonyl-β-alanine the reaction mass was a complex mixture of diverse reaction products from which two tetrahydropyrimidines were isolated—the expected 2-phenyl-4-piperonyl-6-oxotetrahydropyrimidine and 2-methyl-4-piperonyl-6-oxotetrahydropyrimidine. The latter is undoubtedly formed as the result of transacylation, the same as the amide of N-acetyl-β-piperonyl-β-alanine, N-acetyl-β-piperonyl-β-alanine and benzoic acid, which were all isolated from the same reaction mass. In addition, here we also found desamination products—piperonylacrylic acid and diacetamide.



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* Deceased.

Closure of the amides of N-carbomethoxy- and N-acetyl-β-piperonyl-β-alanines gave the corresponding 2-methoxy- and 2-methyl-6-oxotetrahydropyrimidines, but at the same time piperonylacrylic acid was isolated, and in the last case also diacetamide, so that here also there were secondary reactions.

EXPERIMENTAL

Reaction of N-Benzoyl-β-piperonyl-β-alanine with $SOCl_2$ and subsequent treatment with ammonia. A mixture of 10 g of N-benzoyl-β-piperonyl-β-alanine and 9 ml of thionyl chloride was heated at 80° for about 2 hours on the water bath until hydrogen chloride ceased to evolve (after 1 hour the mass began to crystallize). The excess $SOCl_2$ was vacuum distilled, the residual dark crystalline mass treated with ether, and the resulting suspension saturated with ammonia under frequent shaking. The next day the precipitate was filtered, washed with water, alkali solution, again with water and recrystallized from water, and then from alcohol. The yield of previously described piperonylacrylamide [4] with m.p. 184-185° was 4.5 g (70%).

Found %: N 7.69; C 63.33; H 5.00. $C_{10}H_9O_3N$. Calculated %: N 7.33; C 62.83; H 4.71

Reaction of the amide of N-carbomethoxy-β-piperonyl-β-alanine with acetic anhydride. A mixture of 4 g of the amide and 20 ml of acetic anhydride was boiled for 8 hours. Then 16 ml of acetic anhydride was removed by distillation, and the residue boiled for 30 minutes with water and then evaporated to disappearance of acetic acid odor. The residual oil was treated with ether; the ether extract was washed with soda and then with water, and then dried over Na_2SO_4. From the ether-isoluble residue was isolated 0.6 g of starting amide. Removal of ether from the ether solution by distillation gave 2.3 g of viscous dark-yellow oil, which was heated for 20 minutes on the water bath with 5% alkali solution, then extracted with ether, and the ether extract dried over Na_2SO_4. Acidification of the alkaline solution gave 0.5 g of mixed acids, from which by treatment with hot water was isolated 0.2 g of piperonylacrylic acid and 0.1 g of N-carbomethoxy-β-piperonyl-β-alanine. Removal of the ether from the ether extract by distillation gave 1.4 g of oily yellow substance, from which after two recrystallizations from alcohol was isolated 0.9 g of neutral substance with m.p. 80-81°, insoluble in water, soluble in ether, and proving to be 2-methoxy-4-piperonyl-6-oxotetrahydropyrimidine.

Found %: N 11.48; C 57.97; H 4.79. $C_{12}H_{12}O_4N_2$. Calculated %: N 11.29; C 58.06; H 4.84.

Reaction of the amide of N-acetyl-β-piperonyl-β-alanine with acetic anhydride. A mixture of 15 g of the amide and 75 ml of acetic anhydride was boiled for 9 hours, after which the acetic anhydride was vacuum distilled, and the residue was boiled with water for 30 minutes. The oily deposit obtained on cooling the solution was washed several times with water and then treated with chloroform. The chloroform solution was washed with water, soda solution, again with water, and dried over potash. From the water and soda solutions were isolated 0.55 g of starting amide, 1.45 g of N-acetyl-β-piperonyl-β-alanine and 0.95 g of piperonylacrylic acid. From the chloroform solution after distilling off the solvent was obtained an oil, which on standing crystallized as needles. After washing with ether and recrystallization from a mixture of alcohol and ether, or from a mixture of chloroform with either diethyl or petroleum ether, there was obtained 6 g of 2-methyl-4-piperonyl-6-oxotetrahydropyrimidine with m.p. 106-107°.

Found %: N 11.96; C 62.11; H 5.24. $C_{12}H_{12}O_3N_2$. Calcuated %: N 12.07; C 62.07; H 5.17.

The substance is insoluble in water, difficulty soluble in ether, petroleum ether and benzene, and readily soluble in alcohol and chloroform. 2-Methyl-4-piperonyl-6-oxotetrahydropyrimidine differs from other similar 6-oxotetrahydropyrimidines, having either the phenyl or methoxy group substituted in the 2 position (independent of the radical in the 4 position), by being more easily saponified and showing somewhat more basic properties. Thus, the heating of this compound with 5% alkali solution on the water bath for 10 minutes gave N-acetyl-β-piperonyl-β-alanine and its amide, and when heated for 1 hour, N-acetyl-β-piperonyl-β-alanine and piperonylacrylic acid, while usually several hours of heating is required for the alkaline hydrolysis of other 6-oxotetrahydropyrimidines to the amides of the corresponding N-acyl-β-amino acids. 2-Methyl-4-piperonyl-6-oxotetrahydropyrimidine slowly goes into solution when treated with hydrochloric acid (1:1) in the cold: at first it can be recovered unchanged when the solution is made alkaline, but after prolonged treatment in the cold or when heated it suffers hydrolysis to the amide of N-acetyl-β-piperonyl-β-alanine.

2-Methyl-4-piperonyl-6-oxotetrahydropyrimidine fails to give either the picrate or a stable hydrochloride under the usual conditions. Comparative studies revealed that some other 2-methyl-6-oxotetrahydropyrimidines (for example: 2-methyl-4-hexyl-6-oxotetrahydropyrimidine and 2-methyl-4-phenyl-6-oxotetrahydropyrimidine) also dissolve slowly in acid and are precipitated by alkali from acid solution in unchanged form.

Reaction of the amide of N-benzoyl-β-piperonyl-β-alanine with acetic anhydride. A mixture of 10 g of the amide and 50 ml of acetic anhydride was boiled for 10 hours, after which the acetic anhydride was vacuum distilled. Toward the end of distillation colorless needles (0.5 g) of diacetylamide appeared in the outlet tube, m.p. 80-81° (from ether) [5]. The dark-brown oil remaining after distillation was treated several times with chloroform. The residue was 0.1 g of starting amide. The chloroform solution was washed with acid, soda, water, and dried over Na_2SO_4. The oily residue remaing after distilling off the chloroform was treated with ether, where 1.5 g of neutral substance with m.p. 133-136° was isolated. Purification of this substance gave 1g of 2-phenyl-4-piperonyl-6-oxotetrahydropyrimidine with m.p. 150-151° (from alcohol).

Found %: N 9.49; C 69.35; H 5.15. $C_{17}H_{14}O_3N_2$. Calculated %: N 9.52; C 69.39; H 4.76.

The amide of N-acetyl-β-piperonyl-β-alanine was isolated when the acid solution was made alkaline.

The noncrystallizing oil from the alcohol and ether mother liquors was steam distilled. From the distillate was isolated 1.3 g of benzoic acid, while from the residue was obtained 0.5 g of base with m.p. 101-103°, proving to be identical with 2-methyl-4-piperonyl-6-oxotetrahydropyrimidine, and 0.25 g of mixed N-benzoyl-β-piperonyl-β-alanine and piperonylacrylic acid. An attempt to increase the yield of 2-phenyl-4-piperonyl-6-oxotetrahydropyrimidine by replacing the acetic anhydride by either benzoyl chloride or benzoic anhydride failed to give a positive result: with benzoyl chloride under the same conditions closure of the tetrahydropyrimidine ring was completely absent (the product was a tar), while with benzoic anhydride the closure proceeded with only a small yield.

SUMMARY

1. The reaction for the formation of substituted tetrahydropyrimidines from N-acyl-β-piperonyl-β-alanines and their amides was studied. It was established that the heating of N-acyl-β-piperonyl-β-alanines with thionyl chloride at 80°, followed by treatment with ammonia, fails to result in closure of the tetrahydropyrimidine ring. In contrast to other N-benzoyl-β-alkyl(aryl)-β-alanines, giving the corresponding tetrahydropyrimidines under these conditions, N-benzoyl-β-piperonyl-β-alanine shows only desamination, being converted into the amide of piperonylacrylic acid.

2. The reaction of the amides of N-acetyl-, N-carbomethoxy- and N-benzoyl-β-piperonyl-β-alanines with acetic anhydride respectively gave the 2-methyl-, 2-methoxy- and 2-phenyl-6-oxotetrahydropyrimidines. The amide of N-benzoyl-β-piperonyl-β-alanine gave two 6-oxotetrahydropyrimidines, the expected 2-phenyl-4-piperonyl-6-oxotetrahydropyrimidine and 2-methyl-4-piperonyl-6-oxotetrahydropyrimidine (transacylation).

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ISONICOTINOYLACETIC ESTER AND ITS DERIVATIVES

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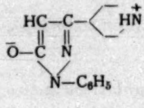
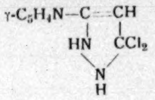
The antitubercular activity [1] shown by the hydrazide of isonicotinic acid, synthesized some 40 years ago [2], and also by its condensation products with aldehydes and ketones [3], has aroused increased interest in derivatives of isonicotinic acid. In connection with this we became interested in the ethyl ester of isonicotinoylacetic acid as a starting substance for the preparation of a number of new physiologically active compounds, including, e.g., 3-(γ-pyridyl)-5-pyrazolone, functioning simultaneously as a hydrazide and as a hydrazone. In its properties, revealed by us in studying its transformations, the isonicotinoylacetic ester differs from the nicotinoylacetic ester described by Clemo [4] in a number of reactions.

Isonicotinoylacetic ester gives stable sodium or potassium salts, which can be crystallized from water solution. This permitted us to simplify the method of obtaining isonicotinoylacetic ester by crystallizing its sodium compound after Claisen condensation and isolating the pure isonicotinoylacetic ester (with m. p. 54°) from the sodium derivative. With hydrazine hydrate the isonicotinoylacetic ester readily forms 3-(γ-pyridyl)-5-pyrazolone, a substance that simultaneously possesses both acidic and basic properties, and consequently shows a high melting point with decomposition. If phenylhydrazine is substituted for hydrazine hydrate in the condensation, then 1-phenyl-3-(γ-pyridyl)-5-pyrazolone is obtained, a grayish-green substance, soluble in aqueous solutions of both alkalies and acids. The color of this compound is apparently due to intramolecular neutralization of the basic pyridine group by the carbonyl, augmented by the nearness of the phenyl group.

This is found to be in agreement with the infra-red spectrum, where the band for the carbonyl group is absent in the 1700-1630 cm^{-1} region and a band is present in the 2450-2500 cm^{-1} region, revealed in crystalline amine hydrochlorides and characteristic for the grouping: $>N-H^{+}$. This is also supported by the fact that its hydrochlorides are nearly colorless. Nitrosation of the obtained pyrazolone gives a cream-colored isonitroso compound, soluble in acid solutions

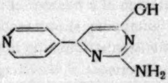


with a brownish-red color and insoluble in alkali solutions, which indicates entrance of the isonitroso group in position 4. Michael and Rassmann [5] converted 3-phenyl-5-pyrazolone into 3-phenyl-5-chloropyrazole by boiling it with $POCl_3$. According to Clemo [4], prolonged heating of 3-(β-pyridyl)-5-pyrazolone with phosphorus pentachloride at 180° also gave the 3-(β-pyridyl)-5-chloropyrazole. We were unable to introduce chlorine into the molecule under these conditions. Apparently, γ-pyridyl substitution stabilizes the pyrazolone molecule much more than does β-pyridyl. Only when phosphorus pentachloride was reacted at 140° were we able to obtain the chloro derivative, which, however, contained 2 chlorine atoms, and apparently was 3-(γ-pyridyl)-5-dichloropyrazole:

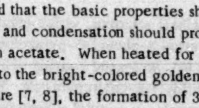


Attempts to obtain the monochloropyrazole by treating the above compound with alcoholic alkali solution proved unsuccessful.

Isonicotinoylacetic ester also condenses easily with guanidine carbonate, forming 4-(γ-pyridyl)-6-hydroxy-2-amino-pyrimidine, a substance with a very high decomposition temperature (357-359°), and nearly insoluble in organic solvents (other than the lower alcohols, in which it is slightly soluble). These properties indicate a high intramolecular neutralization for this compound: 4-(γ-pyridyl)-6-hydroxy-2-aminopyridine is readily soluble in aqueous solutions of alkalies and acids with the separation of well-formed salts. Attempts to replace the hydroxyl group by chlorine using phosphorus oxychloride led to a high-molecular amorphous substance, soluble only in solutions of strong acids.



If isonicotinoylacetic ester is treated with 1 mole of bromine in either chloroform or dilute hydrochloric acid medium and then condensed with thiourea, we obtain 2-amino-4-(γ-pyridyl)-5-carbethoxythiazole in good yield: a microcrystalline yellow powder, with strong hydrochloric acid forming colorless crystals that readily hydrolyze to bright yellow crystals. The substance is saponified when boiled with dilute hydrochloric acid, separating crystals of the colorless hydrochloride. When a solution of this hydrochloride is carefully neutralized it gives a precipitate of 2-amino-4-(γ-pyridyl) thiazole, insoluble in alkali solutions. Such ease of decarboxylation is unusual, since according to the literature [6] 2-amino-thiazole-5-carboxylic acid withstands heating with hydrochloric acid up to 120°. As a result, the influence shown by a substituent with basic properties in position 4 of the thiazole ring appears as a weakening of the carboxyl bond with the 5 carbon atom, the same as in nitrogen-containing heterocycles where the carbon adjacent to the nitrogen atom shows weak bonding with the carboxyl group (2-picolinic acid, 2-thiazole-carboxylic acid, etc.).



Some of the characteristics found when γ-pyridyl substitution is present in heterocycles are also observed for the γ-pyridylisoxazolones. In the condensation of the ethyl ester of isonicotinoylacetic acid with hydroxylamine hydrochloride it could be expected that the basic properties shown by this ester are sufficient to bind the hydrogen chloride of the hydroxylamine, and condensation should proceed. However, it was found that the reaction fails to go without the addition of sodium acetate. When heated for a longer time in alcohol solution the oxime that is formed here suffers cyclization into the bright-colored golden-yellow crystallohydrate of 3-(γ-pyridyl)-5-isoxazolone. According to the literature [7, 8], the formation of 3-phenyl-5-isoxazolone proceeds with considerably greater ease in hydrochloric acid medium. The heating of 3-(γ-pyridyl)-5-isoxazolone with dilute hydrochloric acid (5 N) results in opening of the isoxazole ring, decarboxylation, and formation of the oxime of γ-acetopyridine, proved by the counter synthesis, starting from γ-acetopyridine.

When subjected to biological testing, some bacteriostatic activity toward acid-resistant bacteria was shown by 3-(γ-pyridyl)-5-pyrazolone and 4-(γ-pyridyl)-6-hydroxy-2-aminopyrimidine.

I wish to express deep gratitude to G. N. Pershin and S. N. Milovanova for the biological testing of the compounds prepared by us, and to Yu. N. Sheinker for their spectrographic analysis.

EXPERIMENTAL

Isonicotinoylacetic ester. A molten dispersion of 28 g of sodium in 100 ml of anhydrous xylene was prepared. After cooling most of the xylene was decanted, and the comminuted sodium with residual xylene was transferred by means of 150 ml of dry ether to a three-necked flask with stirrer and reflux condenser, where 56 g of anhydrous alcohol was added in drops. After this the mass was heated with stirring on the steam bath for 3 hours, until all of the sodium was converted into alcoholate. After cooling, a mixture of 182 g of ethyl isonicotinate (b. p. 102.5-103.5° at 14 mm) and 110 g of ethyl acetate was added. At first a suspension of the alcoholate in the mixed esters is formed, but in measure with stirring the mass shows self-heating to 35-40° and becomes a clear, light-red color. Then the mass was heated with stirring on the water bath for 2 hours. After this the ether was distilled off together with the major portion of liberated alcohol. To the residual heterogeneous mass was added 80 ml of water with stirring. On cooling the mass crystallized. After an hour the crystals were separated, washed 3 times with ether, and air-dried. To isolate the isonicotinoylacetic ester the obtained sodio derivative was dissolved in 450 ml of water and acidified with 20% hydrochloric acid at 30-35°. The heavy crystals obtained on cooling were filtered, washed with water, and air-dried. The yield was 155 g. M. p. 53.5-54.5° (54° [9]). Acidification of the alkaline mother liquors and conversion into the Na- derivative gave another 9 g of product. The total yield was 71%.

3-(γ-pyridyl)-5-pyrazolone. In a three-necked flask with stirrer was placed 9.65 g of ethyl isonicotinoylacetate, 25 ml of alcohol and 2.6 g of hydrazine hydrate in 5 ml of alcohol. When heated on the water bath for 1 hour the whole became a white crystalline mass. The crystals obtained here were filtered, and washed twice with alcohol. M. p. 289° (decomp.). Yield 7.6 g (89%). The substance was very slightly soluble in water and alcohol, and readily soluble in solutions of alkalies and acids. After recrystallization from a large volume of water it is obtained as well-formed slender needles. M. p. 291-292.5° (decomp.). Its water solutions are colored yellowish-green. When dissolved in dilute hydrochloric acid and treated with sodium nitrite it gives an intense yellow color, which turns to a red when made alkaline.

Found %: N 25.8. $C_8H_7ON_3$. Calculated %: N 26.2.

White crystals of the hydrochloride are obtained when the substance is dissolved in hot 10% hydrochloric acid and the solution cooled. M. p. about 280° (decomp.).

Found %: Cl 17.5. $C_8H_7ON_3 \cdot HCl$. Calculated %: Cl 17.9.

3-(γ-Pyridyl)-5-dichloropyrazoline. Four grams of 3-(γ-pyridyl)-5-pyrazolone was crushed in a mortar with 5.2 g of phosphorus pentachloride, and the mixture was heated in a flask in an oil bath at 140° for 4 hours. The mass after cooling was treated with ice (100 g). When the solution obtained here was carefully treated with $NaHCO_3$ (to slightly alkaline reaction) a brown precipitate was obtained, which was filtered, washed with water, dried, and extracted with hot benzene. The yield of straw-colored crystalline powder with m. p. 222-224° was 0.8 g. When kept in the air it shows partial efflorescence. After 3-hour boiling with a 2.5% alcoholic KOH solution the dichloride was recovered unchanged with m. p. 221°.

Found %: H_2O 7.6; Cl 30.0, 29.9. $C_8H_7N_3Cl_2$. Calculated %: H_2O 7.7; Cl 30.2.

1-Phenyl-3-(γ-pyridyl)-5-pyrazolone. A solution of 5.7 g of ethyl isonicotinoylacetate in 15 ml of alcohol was heated on the water bath with 4.5 g of phenylhydrazine hydrochloride until complete solution had been achieved. Then a solution of 2.4 g of sodium acetate in 5 ml of water was added. The reaction mass turned yellow-orange, a precipitate of NaCl was obtained, the whole was heated under reflux and with stirring for 2 hours, then the alcohol was distilled off, and the residue was treated with 15 ml of water. After some time the tarry residue crystallized. The crystals were filtered, washed with water, and treated with 25 ml of hot alcohol. On cooling the crystals were again filtered and washed twice with alcohol (in 10 ml portions). The fine crystals were colored a brownish-green. The yield was 4.6 g. For purification the 1-phenyl-3-(γ-pyridyl)-5-pyrazolone was converted into the hydrochloride, which is slightly soluble in water and has a light brown color. M. p. 251-253°.

Found %: Cl 11.4; H_2O 11.1. $C_{14}H_{11}ON_3 \cdot HCl \cdot 2H_2O$. Calculated %: Cl 11.5; H_2O 11.1.

The base was isolated from the hydrochloride and recrystallized from alcohol. Well-formed gray-green crystals were obtained. At 160-170° volatile products are evolved from these crystals; the whole again becomes solid, and then melts at 209-211°.

Found %: H_2O 5.1. $C_{14}H_{11}ON_3 \cdot {}^2\!/_3 H_2O$. Calculated %: H_2O 4.9.

The substance was dried at 100-105°.

Found %: N 17.8, 18.1. $C_{14}H_{11}ON_3$. Calculated %: N 17.7.

2-Amino-4-(γ-pyridyl)-6-hydroxypyrimidine. To a boiling suspension of 10 g of guanidine carbonate in 20 ml of alcohol was gradually added under stirring 12 g of isonicotinoylacetic ester. Carbon dioxide gas was evolved, the whole went into solution, and then a fine white precipitate began to deposit. The heating with stirring was continued for 3 hours, then 2 ml of 40% NaOH was added, the resulting solution filtered, and a white microcrystalline precipitate was isolated by treating the filtrate with acetic acid. Yield 10 g (86%). M. p. 357-359° (decomp.). The substance is very slightly soluble in alcohol and water, and soluble in dilute acids and alkalies.

Found %: N 28.5, 28.4. $C_9H_8ON_4$. Calculated %: N 28.5.

Two grams of 2-amino-4-(γ-pyridyl)-6-hydroxypyrimidine was dissolved under heating in 10% sodium hydroxide solution. On cooling a mass of crystalline needles deposited, which were filtered, washed with alcohol, and dried; readily soluble in water. Yield 3.5 g.

Found %: H_2O 29.0. $C_9H_7ON_4Na \cdot 5H_2O$. Calculated %: H_2O 30.0.

2-Amino-4-(γ-pyridyl)-5-carbethoxythiazole. In a three necked flask with stirrer was placed 7.7 g of ethyl isonicotinoylacetate, and to this was added 40 ml of water and 4 ml of concentrated hydrochloric acid. When stirred the whole went into solution. Then from a micropipet in a period of 10 minutes was added, in drops and with ice-cooling, 2.1 ml of bromine. The cooling bath was removed, and then a solution of 4.6 g of thiourea in 10 ml of water was added dropwise (with some heat evolution). After this the mixture was heated on the water bath at 60-65° for 1.5 hours. The turbidity and small amount of sulfur precipitate obtained here were filtered. The filtrate was neutralized with ammonia until weakly acid to Congo. The resulting needle crystals of the hydrochloride were filtered, washed with water, dissolved in 150 ml of hot water, and precipitated with potash solution. After cooling the very fine yellowish precipitate was filtered, washed with water, alcohol and ether, and vacuum dried. The yield was 7 g (70%). M. p. 274-275° (decomp.). Nearly insoluble in the ordinary solvents. With acids it gives well-crystallized salts that show low solubility in water.

Found %: N 16.8, 17.2; S 13.3, 13.1. $C_{11}H_{11}O_2N_3S$. Calculated %: N 16.8; S 12.8.

The dissolving of 2-amino-4-(γ-pyridyl)-5-carbethoxythiazole in 20% hydrochloric acid and evaporation of the solution at low temperature gave colorless crystals. When vacuum dried over H_2SO_4, and then over fused potassium hydroxide, the crystals had m. p. 231-232° (decomp.). When moistened with either water or alcohol the crystals immediately turned bright yellow (with considerable loss of hydrogen chloride) and became difficultly soluble in cold water, and somewhat more soluble in hot water.

Found %: Cl 12.45. $C_{11}H_{11}O_2N_3S \cdot HCl$. Calculated %: Cl 12.49.

To obtain bright yellow crystals the 2-amino-4-(γ-pyridyl)-5-carbethoxythiazole was dissolved under heating in 5% hydrochloric acid until acid reaction to Congo appeared. On cooling the whole solution became a felt-like mass of yellow crystals, which were separated, washed with water, and air dried. M. p. 227-228° (decomp.).

Found %: H_2O 8.5; Cl 3.92. $C_{11}H_{11}O_2N_3S \cdot {}^1\!/_3 HCl \cdot 1{}^1\!/_2 H_2O$. Calculated %: H_2O 9.3; Cl 4.09.

2-Amino-4-(γ-pyridyl)thiazole. Three grams of 2-amino-4-(γ-pyridyl)-5-carbethoxythiazole hydrochloride was boiled under reflux with 20 ml of hydrochloric acid (d 1.1) for 2 hours. Fine white crystals were obtained on cooling, which were filtered and dried in the air. Weight 2.5 g. Decomposes around 280°. Difficultly soluble in water.

Found %: H_2O 3.2; HCl 27.0. $C_8H_7N_3S \cdot 2HCl \cdot \frac{1}{2}H_2O$. Calculated %: H_2O 3.5; HCl 27.1.

The white precipitate obtained when the substance was titrated with alkali solution was filtered, washed with water and dried. M. p. 270-272° (with darkening). Insoluble in water and alkali solutions.

Found %: N 23.3, 23.3; S 18.0, 17.5. $C_8H_7N_3S$. Calculated %: N 23.6; S 18.0.

5-(γ-Pyridyl)-3-isoxazolone. To a solution of 4.8 g of ethyl isonicotinoylacetate in 20 ml of alcohol were added 1.75 g of hydroxylamine hydrochloride and 2 g of sodium acetate. The mixture was heated under reflux on the water bath for 2 hours. Here a canary-yellow deposit was obtained. It was filtered, washed with water and then with alcohol. It was vacuum dried over H_2SO_4. The yield was 3.6 g. After recrystallization from hot water, m. p. 193-195° (decomp.). Golden-yellow, well-formed, prismatic crystals.

Found %: N 15.0, 15.3; H_2O 14.2. $C_8H_6O_2N_4 \cdot 1\frac{1}{2}H_2O$. Calculated %: N 14.8; H_2O 14.2.

To study the stability of the isoxazolone 1 g of the substance was heated in 5 ml of 5 N hydrochloric acid for 30 minutes on the steam bath, and then the solution in a dish was evaporated to dryness. The residue was dissolved in 3 ml of water and treated with 10% NaOH solution until no more precipitate was obtained. The precipitate was filtered, washed with water and dried. Weight 0.4 g. Cream-colored powder. Recrystallization from hot water using carbon gave lustrous leaflets of light gray-straw color. Yield 0.25 g. M. p. 158-160°. This compound is insoluble in alkali solutions, quite readily soluble in hot water, slightly soluble in cold water, and soluble in alcohol.

Found %: C 62, 62.0; H 5.7, 5.9; N 20.5, 21.0. $C_7H_8ON_2$. Calculated %: C 61.7; H 5.9; N 20.6.

Consequently, the heating of 5-(γ-pyridyl)-3-isoxazolone with hydrochloric acid led to its decarboxylation with the formation of γ-acetopyridine oxime. To prove the identity of the latter we prepared γ-acetopyridine and converted it into the oxime; glistening white leaflets with m. p. 158.5-160.5° (142° [10]). The mixed melting point with our above obtained substance (m. p. 158-160°) failed to be depressed.

SUMMARY

1. Isonicotinoylacetic ester is capable of various condensations with reagents that show activity toward the carbonyl group: hydrazine, phenylhydrazine, guanidine, hydroxylamine; the corresponding heterocyclic systems are formed, substituted with the γ-pyridyl radical.

2. Brominated isonicotinoylacetic ester readily condenses with thiourea, giving 2-amino-4-(γ-pyridyl)-5-carbethoxythiazole, which when heated with dilute hydrochloric acid shows both hydrolysis and decarboxylation, being transformed into 2-amino-4-(γ-pyridyl)thiazole.

3. The entrance of a γ-pyridyl substituent in heterocyclic systems produces essential deviations in chemical properties when compared with aromatic substituents, changing the reaction capacity shown by the functional groups of the heterocycle and also endowing the new compounds with sharply different physical properties.

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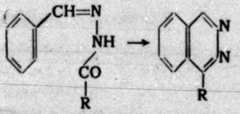
THE SYNTHESIS OF PHTHALAZINES BY THE CYCLIZATION OF THE ACYLHYDRAZONES OF AROMATIC ALDEHYDES

N. K. Kochetkov and L. A. Vorotnikova

Of the methods known in the literature for the synthesis of phthalazine derivatives the method of cyclizing acylhydrazones of aromatic aldehydes in accord with the following scheme attracts attention:



This reaction was described in 1929 by a group of Indian chemists [1, 2] and is given as a general method for the synthesis of phthalazines in reviews [3] and monographs [4]. After the above paper was published in the literature there apparently was no more data dealing either with the expansion of this method or a verification of the published results.

Having in mind the preparation of a number of phthalazine derivatives, we decided to make use of the indicated reaction. The study was begun with a cyclization of the acetylhydrazone of veratraldehyde under the influence of hydrogen chloride in anhydrous isoamyl alcohol solution, as is recommended by the authors [1]. As a reaction result a substance with m. p. 191-193° was isolated, which in accord with the scheme given above should be 1-methyl-6,7-dimethoxyphthalazine. However, study revealed that in its properties the substance cannot be classified as a compound of the phthalazine series. Thus, it failed to give a methiodide even under drastic conditions, and its salts with mineral acids are instantaneously hydrolyzed by water, although it is known that phthalazines give fully stable methiodides [5, 6] and salts [7, 8]. The properties and analysis of the obtained compound indicated that actually it is the azine of veratraldehyde. This was confirmed by its direct comparison with an authentic specimen of the azine via the mixed melting point test.

A detailed examination of the above cited papers revealed that the substances obtained by the authors fail to show sufficiently complete and fully satisfactory analyses; together with this the indicated compounds, regarded as being phthalazine derivatives, in their melting points lie exceedingly close to the azines of the corresponding starting aldehydes (see table).

It is evident that the reaction products are actually not phthalazines, but the corresponding azines. We also confirmed this conclusion on the example of treating the benzoylhydrazone of anisaldehyde with hydrogen chloride in isoamyl alcohol. The substance obtained here, in its melting point coinciding with that described by the authors for 1-phenyl-7-methoxyphthalazine, proved to be actually the azine of anisaldehyde. In exactly the same manner the substance obtained in the "cyclization" of the benzoylhydrazone of veratraldehyde proved to be not 1-phenyl-6, 7-dimethoxyphthalazine, but instead the azine of veratraldehyde. We were finally convinced of this when we took the ultraviolet absorption spectrum of the obtained substance, which proved to be completely identical with the spectrum of authentic veratraldehyde azine (Fig. 1).

To elucidate its actual course the reaction was studied in detail on the example of the benzoylhydrazone of of veratraldehyde. After its treatment with hydrogen chloride in anhydrous isoamyl alcohol, together with the

Starting substance	Structure of the reaction product based on the data of the authors and its melting point [1, 2]	Melting point of the azine of the corresponding aldehyde
Veratraldehyde benzoylhydrazone	1-Phenyl-6,7-dimethoxyphthalazine (193°)	Veratraldehyde azine (191°) [9]
Veratraldehyde phenacetylhydrazone	1-Benzyl-6,7-dimethoxyphthalazine (191-192°)	
Veratraldehyde veratroylhydrazone	1-Veratryl-6,7-dimethoxyphthalazine (192-193°)	
Anisaldehyde benzoylhydrazone	1-Phenyl-7-methoxyphthalazine (167°)	Anisaldehyde azine (168°) [10]
Anisaldehyde phenacetylhydrazone	1-Benzyl-7-methoxyphthalazine (168-169°)	
Piperonal benzoylhydrazone	1-Phenyl-6,7-methylenedioxyphthalazine (200°)	Piperonal azine (201.5°) [11]
Piperonal phenacetylhydrazone	1-Benzyl-6,7-methylenedioxyphthalazine (202°)	

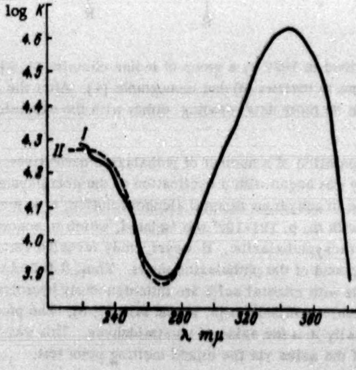


Figure 1. Ultraviolet absorption spectra of veratraldehyde azine (I) and the substance obtained from veratraldehyde benzoylhydrazone (II).

azine of veratraldehyde, isoamyl benzoate was isolated from the reaction mixture, which was confirmed by its hydrolysis, leading to benzoic acid. It should be mentioned that also in the treatment of the acetylhydrazone of veratraldehyde the characteristic odor of isoamyl acetate appears in the reaction mixture. Evidently, the treatment of acylhydrazones of aromatic aldehydes under these conditions leads not to cyclization, but instead reduces to alcoholysis of the acyl radical in the presence of hydrogen chloride and subsequent disproportionation of the liberated hydrazone into the azine [12]:

$$\mathrm{ArCH{=}NNHCOR} + \mathrm{C_5H_{11}OH} \xrightarrow{\mathrm{HCl}} \mathrm{RCOOC_5H_{11}} + \mathrm{ArCH{=}NNH_2} \longrightarrow \mathrm{ArCH{=}N{-}N{=}CHAr}.$$

Such a course for the reaction is close to that known from the literature for the hydrolysis of acylhydrazones in the presence of hydrochloric acid [13]. The obtained results arouse re-examination of some of the conclusions made relative to the seeming anomalies shown by the properties of phthalazine derivatives, which conclusion was reached on the basis of studying the properties of the obtained compounds, since actually these facts fail to relate to phthalazine derivatives.

EXPERIMENTAL

Reaction of veratraldehyde acetylhydrazone with hydrogen chloride in isoamyl alcohol. One gram of veratraldehyde acetylhydrazone in 10 ml of anhydrous isoamyl alcohol was saturated at 0° with dry hydrogen chloride, then heated for 1 hour on the water bath and boiled for 1 hour. After cooling the precipitate was filtered; recrystallization from alcohol gave 0.46 g of substance as yellow needles with m. p. 191-193°. Its mixed melting point with veratraldehyde azine [9] failed to be depressed.

Found %: C 66.07, 65.99; H 6.16, 6.21. $C_{18}H_{20}O_4N_2$. Calculated %: C 65.83; H 6.13.

Reaction of anisaldehyde benzoylhydrazone with hydrogen chloride in isoamyl alcohol. The reaction with 0.7 g of anisaldehyde was run in a similar manner. There was isolated 0.25 g of substance as yellow needles with m. p. 167-168°. Its mixed melting point with anisaldehyde azine [10] failed to be depressed.

Found %: N 10.66, 10.67. $C_{16}H_{16}O_2N_2$. Calculated %: N 10.44.

Reaction of veratraldehyde benzoylhydrazone with hydrogen chloride in isoamyl alcohol. Twenty grams of vertraldehyde benzoylhydrazone in 200 ml of anhydrous isoamyl alcohol, saturated with dry hydrogen chloride, was heated for 1 hour on the water bath and 1 hour at the boil. On cooling the precipitate was filtered; recrystallization from alcohol gave 9.5 g of yellow needles with m. p. 191-193°. Its mixed melting point with veratraldehyde azine, and also with the substance obtained from the acetylhydrazone, failed to be depressed.

The alcohol was removed from the filtrate by distillation, the residue was extracted with ether, the extract was dried over sodium sulfate, the ether was removed, and the residue was vacuum distilled. There was obtained 6.8 g of substance with b. p. 104-104.5° (5 mm), n_D^{20} 1.4939.

Literature for isoamyl benzoate [14]: b. p. 260.7°.

Hydrolysis of 2 g of the obtained substance by boiling with 20 ml of hydrochloric acid for 10 hours gave 1.05 g of benzoic acid, which after distillation had m. p. 121°. Its mixed melting point with an authentic specimen failed to be depressed.

SUMMARY

It was shown that the treatment of acylhydrazones of aromatic aldehydes with hydrogen chloride in isoamyl alcohol leads not to phthalazine derivatives, as was believed earlier, but instead to the azines of the corresponding aldehydes.

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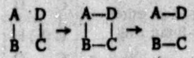
THE SEQUENCE OF THE HYDROGENATION, CYCLIZATION AND HYDROGENOLYSIS REACTIONS OF FURAN DERIVATIVES ON NICKEL CATALYSTS

A. A. Balandin and A. A. Ponomarev

The hydrogenation of furan compounds is a new and important phase in the industrial utilization of agricultural wastes [1], for which reason establishing the theoretical rules of this process is of practical interest. The examined reactions are selective; this latter property depends on the nature of the catalysts [1]. To study the indicated problems we resorted to the multiplet theory of catalysis [2]. Nickel is examined below as the catalyst, for which a majority of bond energies needed for the calculations by the multiplet theory is known.

The examined reactions on the surface belong to the doublet type of reactions. In the general scheme for the latter [3]



$$\begin{matrix} A & D \\ | & | \\ B & C \end{matrix} \rightarrow \begin{matrix} A - D \\ | \quad | \\ B - C \end{matrix} \rightarrow \begin{matrix} A - D \\ \\ B - C \end{matrix} \qquad (1)$$

we successively replace the bonds A–B and C–D by bonds that show concrete reaction. Here H–H reacts with the bonds C=C, C=O, C–C C–O and with the bonds in the furan ring C=C (f) and C–O (f) and C=C reacts with O–H (Tables 1 and 2). It is specifically these portions of the molecule that are turned toward the nickel. Here the influence of substituents [4] fails to show decisive significance.

For each reaction of Scheme (1) a broken ("volcanolike") line is constructed [5] – the height of the energy barrier of reaction E as a function of the adsorption potential q. Here

$$E' = \frac{u}{2} - \frac{s}{2} + q \quad \text{(ascending branch E)}, \qquad (2)$$

$$E'' = \frac{u}{2} + \frac{s}{2} - q \quad \text{(descending branch E)}, \qquad (3)$$

where

$$u = -Q_{AB} - Q_{CD} - Q_{AD} + Q_{BC}, \qquad (4)$$

$$s = Q_{AB} + Q_{CD} + Q_{AD} + Q_{BC}, \qquad (5)$$

$$q = Q_{AK} + Q_{BK} + Q_{CK} + Q_{DK}. \qquad (6)$$

Here u is the heat effect of Reaction (1), s is the sum of the energies of the ruptured and formed bonds, and q is the bond energy of the atoms reacting with the catalyst. The letters affixed to the Q bond energies correspond to Scheme (1). The peaks of the broken lines simultaneously set the conditions

$$E_0 = \frac{u}{2}, \qquad (7)$$

$$q_0 = \frac{s}{2}, \qquad (8)$$

while the broken lines themselves descend from the peaks at an angle of ± 45° to the abscissa, as can be seen from Equations (2) and (3). The broken lines depend on the reaction nature, but not on the catalyst. E' is the energy of formation of the intermediate multiplet complex from the starting substances and catalyst; in Fig. 1

TABLE 1

Sequence of Reactions in Hydrogenation Over Ni

Reaction No.	Reaction	Scheme	u	s	E'
1	Hydrogenation of an olefinic bond	$\begin{matrix} C & H \\ \Vert & \vert \\ C & H \end{matrix}$	30.1	331.9	− 2.9
2	Hydrogenation of a carbonyl bond	$\begin{matrix} C & H \\ \Vert & \vert \\ O & H \end{matrix}$	13.5	388.7	−10.1
3	Hydrogenation of the first double bond in the furan ring	$\begin{matrix} C & H \\ \Vert & \vert \\ C(f) & H \end{matrix}$	14.1	347.9	−10.9
3a	Hydrogenolysis of an ether bond in the furan ring	$\begin{matrix} C & H \\ \vert & \vert \\ O(f) & H \end{matrix}$	3.8	398.4	−11.8
4	Formation of a spiran from a furan alcohol	$\begin{matrix} C & O \\ \Vert & \vert \\ C & H \end{matrix}$	10.3	324.9	−15.8
5	Hydrogenolysis of a carbon-oxygen bond	$\begin{matrix} C & H \\ \vert & \vert \\ O & H \end{matrix}$	19.8	382.4	−16.8
6	Hydrogenolysis of a carbon-carbon bond	$\begin{matrix} C & H \\ \vert & \vert \\ C & H \end{matrix}$	10.6	351.4	−48.4

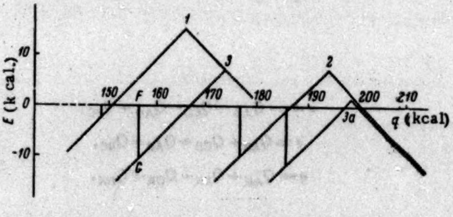


Figure 1. Height of the energy barrier E of Reactions 1, 2, 3 and 3a (Table 1) as a function of the adsorption potential q.

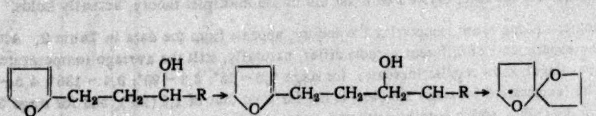
it corresponds to the section FG. The greater E', the easier, i.e. at a lower temperature the reaction proceeds, since the energy of activation $\epsilon \approx -\frac{3}{4}E'$. However, E' cannot be greater than half the reaction heat u [see Equation (7)], which is important later. Adsorption factors are practically without influence; apparently, the kinetics order of the examined reactions on Ni is close to zero.

In order to use Equations (2)-(8) it is necessary to know the bond energies. For reactions capable of progress in the hydrogenation of furan compounds, we find u and s from Equations (4) and (5), utilizing the bond energies obtained from the data summarized by Cottrell [6], and also from the data of [7]: $Q_{H-H} = 104.2$, $Q_{O-H} = 110.6$, $Q_{O-C} = 77.1$; $Q_{C-C} = 66.2$, for the bonds that react first $Q_{C-C} = 46.7$, $Q_{C-O} = 83.4$ (average for aldehyde and ketone); the value of the energy of stabilization for furan $\sigma = 16$ was assumed in accord with [8]. The latter should be added to the first rupturing bond in the furan cycle. The values of u and s calculated in this manner are given in Table 1. The numbers of the reactions in Table 1 are retained unchanged to the end of the paper. The energy values are always given in kcal./mole. The values of u and s, given in Table 1, permit construction of the "volcanolike" curves (Fig. 1, for Reactions 1, 2, 3 and 3a). Due to the presence of energy of stabilization the peak of Reaction 3 lies considerably below the peak of Reaction 1. This indicates that Reaction 3 should have a lower E' and should proceed with greater difficulty than Reaction 1. E' was calculated on the basis of Equation (2); into it enter those values of u and s that were mentioned above, and in addition, the adsorption potentials q. We calculate the values of q from the values of the bond energies Q_{ANi}, given in Reference [7] for the general case: $Q_{C-Ni} = 6$, $Q_{=C-Ni} = 19$, $Q_{H-Ni} = 55$, $Q_{O-Ni} = 48.5$ (here $=C$ denotes a carbon atom linked to a double bond). In the hydrogenation of the bonds $C=C$ (f) and $C-O$ (f) we assume that the intermediate active complex, into whose composition enters a deformed furan cycle, still contains half of the energy of stabilization $\sigma/2 = 8$. The values of E', calculated from Equation (2), are given in Table 1, where the reactions are arranged in the order of decreasing E', i.e. in the order of increasing difficulty of progress. As a result, with the aid of the multiplet theory it is possible to find a rule, in accord with which, depending on their difficulty of progress, the reactions for the hydrogenation of furan compounds can be arranged in a definite order.

Thus, for example, the found rule requires that in the hydrogenation of 1-(α-furyl)-1-penten-3-one over Ni there should be formed in sequence: 1) 1-(α-furyl)-3-pentanone (similar to No. 2, Table 2), 2) 1-(α-furyl)-3-pentanol, 3) 1-(α-tetrahydrofuryl)-3-pentanol (No. 20, Table 2), 4) 2-ethyl-1,6-dioxa-4,4-spirononane (No. 69, Table 2), and then, through a number of uniform successive stages, 5) n-nonane and, finally, 6) methane.

As the data in Table 1 show, actually the ether bond $C-O$ (f) fails to participate in the transformations on Ni for the reason that the $C=C$ (f) bond shows prior hydrogenation, as a result of which the $C-O$ (f) bond vanishes, being automatically transformed into a $C-O$ bond, and then its reactions should be considered together with the reactions of the latter. Due to the close proximity of E' for Reaction 3 and 3a (Table 1) the possibility is not excluded of Reaction 3a also showing a slight degree of progress on Ni.

We will discuss the formation of spirans from furan alcohols. As was experimentally shown earlier [10], here an intermediate compound is formed, in which a H_2 molecule is added to one (external) $C=C$(f) bond (E' = −10.9), and then the side chain shows bending, and Reaction 4 takes place with the formation of the spiran (E' = −15.8), but the $C-O$ still fails to show rupture (E' = −16.8), in accord with the requirements of Table 1:



(9)

When the first H_2 molecule adds, then the $C=C$(f) bond shows hydrogenation, and here the system of a furan nucleus disappears, while when a new ring shows closure, then since the furan system had disappeared, the $O-H$ bond now adds to the ordinary $C=C$ bond, as was indicated in Table 1.

The addition of $O-H$ to a carbon-carbon double bond is most frequently an ionic reaction, as can be seen from the favorable influence exerted on it when the hydrogen ion concentration is increased. However, instead of being ionic, this reaction can also be surface-atomic. On nickel, as shown experimentally, the acidity fails to influence the formation rate of the spiran [11]. Consequently, the reaction fails to be ionic, and it is lawful to apply to it the calculation method of Table 1.

Parallel with the formation of the spiran, the intermediate dihydrofuran alcohol is hydrogenated to the tetrahydrofuran alcohol by Reaction 1. Progress of the latter, when compared with Reaction 4, is facilitated by a higher E', but is retarded by the fact that it is bimolecular, while Reaction 4 is monomolecular.

Verification of the found rule (Table 1) on experimental data is given in Table 2, where the experimental material on the sequence of reactions in the hydrogenation of furan compounds on nickel is collected, and from which it can be seen that the found rule is observed experimentally. This evaluation can be made directly, comparing the data of Table 2 for each compound in Table 1. The exceptions are few; they are designated by asterisks. To avoid being arbitrary, all of the data found in the literature on the hydrogenation of furan compounds (about 100 transformations) are given in Table 2, with the exception of acids and their esters (due to the known and confirmed here special stability of the carboxyl group), and also nitrogen compounds (due to the paucity of data). For furfurol we took the results of recent studies (see No. 58, Table 2), and not the old [54, 55], due to the absence of faith in the Ni purity. The lack of change for the hydrocarbon radicals R in Table 2 ensues from theory.

It is essential that variation in the methods of Ni preparation (NiK – nickel on kieselguhr, NiS – skeletal), temperature and pressure fail to exert an influence within the study limits of the found sequence of reactions.

A systematic method of checking is given below, permitting avoidance of subjective errors, which can arise in the examination of such diverse material. Let A = 123, 456 denote that Reactions 1, 2 and 3 in Table 1 have already taken place, and Reactions 4, 5 and 6 have not (for example, see No. 34 in Table 2). In A some of the numbers can be absent, if the molecular structure is such that the given reactions are impossible (for example, Reaction 4 in the case of furfurol). The order of the numbers on one side of the comma is immaterial (we place them in increasing order), and on different sides of the comma it is important, since it shows that each of the Reactions 4, 5 and 6 proceeds with greater difficulty than does each of Reactions 1, 2 and 3. Here the reaction went to the 3,4-stage. We write similar expressions of A for the other cases. Some of the primary reactions entice the progress of secondary reactions (we designate the numbers of the latter in italics): 1 → *6*; 2 → *5*; 3 → *1*, *4* and *6*; 4 → *5* and *6*.

Thus, the hydrogenation of the C=O bond (Reaction 2) results in the appearance of the C–O bond, which can then suffer hydrogenolysis (Reaction *5*). Several identical primary or secondary reactions in different parts of the molecule we designate by one number, which is repeated (on different sides of the comma) if all of the one-type reactions have failed to take place. Those reactions that depend on reactions that have failed to take place are not shown in A.

And thus, if the numbers in the stage to which the reaction has gone, or, which is the same, if all of the numbers in expression A go in increasing (or nondiminishing) order, then this means that the rule of Table 1 is observed. For its detailed experimental proof it is necessary for the indicated sequence of numbers in A to hold for the reactions that terminate in the stages 1,2; 2,3; 3,4; 4,5; 5,6. Stoppages of the reactions at the 1,3-type of stages serve as confirmation.

From the data in Table 2 it can be seen that with a few exceptions the numbers in A proceed in increasing order, and consequently the rule, derived with the aid of the multiplet theory, actually holds.

Still another striking result, supporting the theory, appears from the data in Table 2. Although the temperatures in the experiments of different authors differ, naturally, still the average temperatures, required to attain the higher stages, show regular increase: for stage 1,2 – 25°; 2,3 – 90°; 3,4 – 135°; 4,5 – 140°; 5,5 – 210°; 5,6 – 300°. The temperature for stage 1,3 (40°) is not far from that of 1,2 (25°), and for stage 3,5 (130°) not far from that of 3,4 (135°), which is to be expected. We wish to emphasize that the indicated average temperatures are highly approximate, but the general rule of their increase in the reaction series 1-6 is without doubt. The fact that different authors worked independently of each other and set themselves other, preparative, goals, makes observance of this rule all the more striking.

The more difficult hydrogenation of the benzene ring when compared with the furan nucleus, observed constantly (see Nos. 25, 26, 27, 33, 38, 47, 53, 72, 76, 87, 88, Table 2), finds its explanation from such considerations as are given above. To hydrogenate the first bond in benzene (benzene → cyclohexadiene)

TABLE 2

Reaction Sequence for the Hydrogenation of Furan Compounds on Nickel
Comparison of Experimental and Theoretical Data
Designations: F = α-furyl, THF = α-tetrahydrofuryl; NiS = skeletal nickel, NiK = nickel on kieselguhr

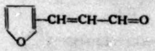
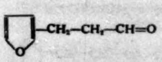
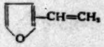
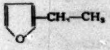
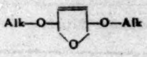
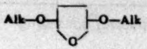
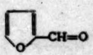
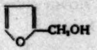
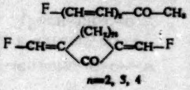
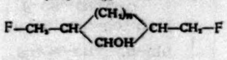
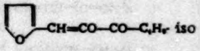
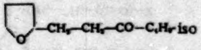
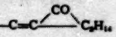
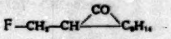
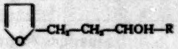
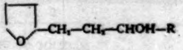
Transformation No.	Starting substance	Substance formed	*A*	Catalyst	Temperature	*P* atm	Literature
1	2	3	4	5	6	7	8
	Transformations going to the 1,2-stage (average temperature 25 °)						
1			1.236	NiC	23°	100	[12]
	F—CH=CH—(C=O)—R	F—CH_2—CH_2—(C=O)—R					
2	R=CH_3	R=CH_3	1.236	NiC	20	50	[14]
3	R=C_6H_{13} iso	R=C_6H_{13} iso	1.236	NiC	20	1	[15]
4	F—$(CH=CH)_2$—(C=O)—CH_3	F—$(CH_2$—$CH_2)_2$—CO—CH_3	1.236 1.236	NiC Ni	20 —	1 —	[16] [17]
5	F—CH=CH—CO—F	F—CH_2—CH_2—CO—F	1.236	NiC	42	100	[18]
6	$(F$—$CH=CH)_2C=O$	$(F$—CH_2—$CH_2)_2C=O$	1.236	NiC	20	1	[19]
	Transformations going to the 1,3-stage (average temperature 40 °)						
7			1.36 1.36	NiK NiC	65 15	250 75	[20] [4C]
8	F—CH=CH—CH_2OH	F—CH_2—CH_2—CH_2OH	1.356	Ni	—	—	[12]
	Transformations going to the 1,5-stage (average temperature 25 °)						
9			1.56	NiC NiK	25	1.5	[21]

TABLE 2 (Continued)

Transformation No.	Starting substance	Substance formed	A	Catalyst	Temperature	P atm	Literature
1	2	3	4	5	6	7	8
Transformations going to the 2,3-stage. Average temperature 90 °							
10			2.356	Ni	160	65	[22]
		F—CH₂OH F—CH₃	25.36*	Ni	185	2	[23]
11	$F-CH=CH-CH=O$	$F-CH_2-CH_2-CH_2OH$	12.356	NiC	80	—	[24]
12	$F-(CH=CH)_2-CO-CH_3$	$F-(CH_2-CH_2)_2-CHOH-CH_3$	12.356	NiC	20	1	[16]
13 14 15	 F —CH=C (CH₂)ₙ C=CH—F CO n=2, 3, 4	 F—CH₂—CH (CH₂)ₙ CH—CH₂—F CHOH	12.356	NiC	20	1	[20]
Transformations going to the 3,2-stage *							
16	 O CH=CO—CO—C₄H₉- iso	 O CH₂—CH₂—CO—C₄H₉-iso	13.256*	Ni			[17]
17	 F—C=C CO C₉H₁₄	 F—CH₂—CH CO C₉H₁₄	13.246*	Ni	—	—	[28]
Transformations going to the 3,4-stage. Average temperature 135 °.							
	 O CH₂—CH₂—CHOH—R	 O CH₂—CH₂—CHOH—R					
18	R = H	R = H	13.456	NiK NiC	87 160	150 110	[11] [12]
19	$R = CH_3$	$R = CH_3$	13.456	NiK	105	150	[21]
20	$R = C_2H_5$	$R = C_2H_5$	13.456	NiK	120	96	[27]
21	$R = C_3H_7$	$R = C_3H_7$	13.456	NiK	120	128	[27]
22	$R = C_4H_9$	$R = C_4H_9$	13.456	NiK	120	99	[27]
23	$R = C_5H_{11}$	$R = C_5H_{11}$	13.456	NiK	120	150	[27]

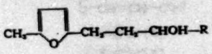
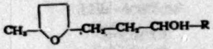
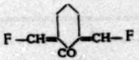
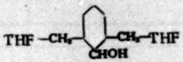
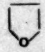
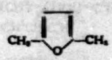
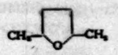
24	$R = C_8H_{17}$ iso	$R = C_8H_{17}$ iso	13.456	NiK	120	103	[27]
25	$R = C_6H_5$	$R = C_6H_5$	13.456	NiK	125	142	[27]
26	$R=CH_2CH_2C_6H_5$	$R=CH_2CH_2C_6H_5$	13.456	NiK	120	142	[27]
27	$F-CH_2CH(CH_3)-CHOH-C_6H_5$	$THF-CH_2-CH(CH_3)-CHOH-C_6H_5$	13.456	NiK	140	110	[27]
28	$(F-CH_2-CH_2)_2CHOH$	$(THF-CH_2-CH_2)_2CHOH$	13.456	NiC	122	105	[28]
							
29	$R=H$	$R=H$	13.456	NiK	120	150	[10]
30	$R=CH$	$R=CH_3$	13.456	NiK	120	137	[10]
31	$F-CH_2CH_2-CH=O$	$THF-CH_2-CH_2-CH_2OH$	123.456	NiK	160	150	[12]
32	$F-CO-CH_2-CO-CH_3$	$THF-CHOH-CH_2-CHOH-CH_3$	123.456	NiC	125	175	[24]
33	$F-CO-CH_2-CO-C_6H_5$	$THF-CHOH-CH_2-CHOH-C_6H_5$ $THF-CHOH-CH_2CH_2-C_6H_5$	123.456 1235.56	NiC	115	175	[24]
34	$F-CH=CH-CH=O$	$THF=CH_2CH_2-CH_2OH$	123.456	NiC N C	160 175	150 150	[12] [29]
35	$F-CH=C(C_2H_5)-CH=O$	$THF-CH_2-CH(C_2H_5)-CH_2OH$	123.456	NiC	175	150	[29]
	$F-CH=CH-CO-R$	$THF-CH_2-CH_2-CHOH-R$					
	$R=CH_3$	$R=CH_3$	123.456	NiC NiC NiC	125 150 175	100 150 150	[30] [12] [29]
36	$R=CH_3$	$THF-CH_2-CH_2CHOHCH_3$ $THF-CH_2-CH_2-CO-CH_3$	123.456 13.2456*	Ni	130	—	[31]
37	$R=C_3H_7$	$R=C_3H_7$	123.456	NiC NiK	200 120	70 148	[16] [16]
38	$R=C_6H_5$	$R=C_3H_7$ $THF-CH_2-CH_2-CH_2-C_6H_5$	123.456 1235.56	NiK	135	150	[12]
39	$F-CH=CH-CO-F$	$THF-CH_2-CH_2-CHOH-THF$	123.456	NiC	130	115	[18]
40			123.456	NiC	175	150	[32]

TABLE 2 (Continued)

Transformation No.	Starting substance	Substance formed	*A*	Catalyst	Temperature	P atm	Literature
1	2	3	4	5	6	7	8
Transformations going to the 3,5-stage. Average temperature 130°							
41			13.56	Ni	195	70	[23]
				NiAl	120	—	[33]
				NiC	80	50	[34]
				NiC	125	100	[32]
				Ni—Al_2O_3	160	60	[35]
		 $CH_3—CH_2—CH_2—CH_2OH$	13.56 135.56	Ni	170		[36]
	F–R	THF –R					
42	R=CH_3	R=CH_3	13.56	NiK	150	100	[24]
				NiC	80	>100	[37]
				Ni	195	70	[23]
				NiAl	120	—	[33]
				NiC	200	—	[38]
				Ni	120	—	[39]
43	R=C_2H_5	R=C_2H_5	13.56	NiC	110	80	[40]
44	R=C_3H_7(n)	R=C_3H_7(n)	13.56				
45	R=C_5H_{11}(n)	R=C_5H_{11}(n)	13.56				
46	F—CH=CH—C_2H_5	THF –$(CH_2)_3CH_3$	13.56	NiC	110	80	[40]
47	F –CH_2—C_6H_5	THF –CH_2—C_6H_5	13.56				
48	 F–CHOH—R	 THF –CHOH—R	13.56	Ni	195	70	[27]

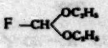
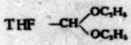
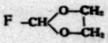
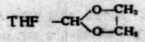
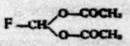
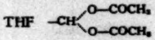
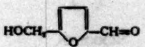
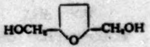
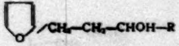
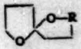
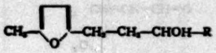
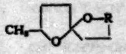
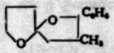
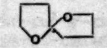
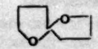
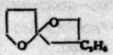
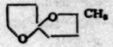
49	R=H	R=H	13,56	NiC	170	100	[41]
				N —Al_2O_3	152	50	[42]
				NiC	80	80	[43,37]
50	R=CH_3	R=CH_3	13,56	NiC	75	10	[44]
					67	80	[43]
51	R=C_2H_5	R=C_2H_5	13,56	NiC	67	80	[43]
52	R=C_3H_7	R=C_3H_7	13,56				
53	R=C_6H_5	R=C_6H_5	13,56				
54	F $-CH_2(CH_2)_3-CHOH-CH_3$	THF $-CH_2(CH_2)_3-CHOH-CH_3$	13,56	NiK	120	90	[15]
55	 F $-CH(OC_2H_5)_2$	 THF $-CH(OC_2H_5)_2$	13,56	NiK	175	—	[24]
		THF $-CH_2-OC_2H_5$	135,56	NiK	175	—	[24]
56			13,56	NiC	125	150	[29]
57	 F $-CH(O-COCH_3)_2$	 THF $-CH(O-COCH_3)_2$	13,56	NiC	160	150	[12]
		THF $-CH_2-O-COCH_3$	135,56				
		THF $-CH_3$	135,56				
58	F $-CH=O$	THF $-CH_2-OH$	123,56	NiC	170	75	[46]
				NiK	155	—	[47]
				Ni	120	140	[48]
				NiK	125	40	[49]
	F $-CH=O$	THF $-CH_2OH$	123,56	Ni	130	90	[31,50]
		THF $-CH_3$	25,1356				
		THF $-H$	1235,56*				
		amylene glycol	1235,56				

TABLE 2 (Continued)

Transformation No.	Starting substance	Substance formed	*A*	Catalyst	Temperature	P atm	Literature
1	2	3	4	5	6	7	8
	F –(CH=CH)$_2$–CO–R	THF–(CH$_2$)$_4$–CHOH–R					
59	R=H	R=H	123,56	NiC	175	150	[29]
60	R=CH$_3$	R=CH$_3$	123,56	NiC	175 200	150 100	[29] [16]
61	R=C$_2$H$_5$	R=C$_2$H$_5$	123,56	NiC	140	100	[14]
62	(F–CH=CH–CH=CH)$_2$C=O	(THF–CH$_2$–CH$_2$–CH$_2$–CH$_2$)$_2$CHOH	123,56	NiC	175	185	[29]
63			723,56	NiC	160	78	[45]
64	F –CHOH–CO–F	(THF–CHOH)$_2$	723,56	NiK	150	150	[12]

Transformations going to the 4,5-stage. Average temperature 140 °
(Proceed mutually with Nos. 18-31, 34-36)

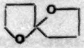
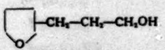
							
65	R=H	R=H	734,56	NiK	97	150	[11]
66	R=CH$_3$	R=CH$_3$	734,56	NiK	105	150	[11]
67	R=C$_2$H$_5$	R=C$_2$H$_5$	734,56	NiK	120	96	[27]
68	R=C$_3$H$_7$	R=C$_3$H$_7$	734,56	NiK	120	128	[27]
69	R=C$_4$H$_9$	R=C$_4$H$_9$	734,56	NiK	120	99	[27]
70	R=C$_5$H$_{11}$	R=C$_5$H$_{11}$	734,56	NiK	120	150	[27]
71	R=C$_8$H$_{17}$, iso	R=C$_8$H$_{17}$, iso	734,56	NiK	120	103	[27]
72	R=C$_6$H$_5$	R=C$_6$H$_5$	734,56	NiK	125	142	[27]
73	R=CH$_2$CH$_2$·F	R=CH$_2$CH$_2$·THF	734,56	NiC	122	105	[28]

74	 R=H	 R=H	734,56	NiK	120	150	[10]
75	R=CH_3	R=CH_3	734,56	NiK	120	137	[10]
76	F—CH_2—CH(CH_3)—CHOH—C_2H_5		734,56	NiK	140	110	[27]
77	F —CH_2—CH_2—CH=O		734,56	NiK	160	150	[12]
78	F —CH=CH—CH=O		1234,56	NiC	160 175	150 150	[12] [29]
79	F —CH=C(C_2H_5)—CH=O		1234,56	NiC	175	150	[29]
80	F-CH=CH—CO—CH_3		1234,56	NiC	—	150	[29]

Transformations going to the 5,5-stage. Average temperature 210 °

81		$CH_3—CH_2—CH_2—CH_2OH$	5,56	NiC	90	155	[31]

TABLE 2 (Continued)

Transformation No.	Starting substance	Substance formed	A	Catalyst	Temperature	P atm	Literature
1	2	3	4	5	6	7	8
82	see No. 41	$CH_3—CH_2—CH_2—CH_2OH$	135,56	Ni	170	—	[36]
83	F $—CH_3$ see No. 42	$CH_3—CH_2—CH_2—CHOH—CH_3$	135,56	NiC	200	—	[38]
84	THF $—CH_2OH$	THF$—CH_3$	5,56	Ni	300	90	[22]
		THF$—H$	56,56*				
		$CH_3—CH_2—CH_2—CH_2OH$	56,56*				
85	F$—CH_2OH$	THF$—CH_3$	135,56	Ni	300	90	[22]
		THF$—H$	1356,56				
		$CH_3—CH_2—CH_2—CH_2OH$	1356,56				
86	F $—CH{=}O$	$CH_2OH—CHOH—CH_2—CH_2—CH_3$	1235,56	NiK	210	40	[49]
		$CH_2OH—CH_2—CH_2—CH_2—CH_2OH$	1235,56				
		$CH_3—CH_2—CH_2—CH_2—CH_2OH$	1235,56				
87	F $—CH{=}CH—CO—C_6H_5$	THF$—(CH_2)_3—C_6H_5$	1235,56	NiC	140	135	[27]
88	F $—CH{=}C(CH_3)—CO—C_6H_5$	THF$—CH_2—CH(CH_3)—CH_2—C_6H_5$	1235,56	NiC	135	125	[27]
89	THF$—CH_3$	$CH_3—CH_2—H_2—CHOH—CH_3$	5,56	Ni	330	140	[52]
90		THF$—(CH_2)_2—CH_2OH$	5,56	NiK	200°	150	[13]
Transformations going to the 5,6-stage. Average temperature > 300°							
91		THF$—C_3H_7$	5,56	NiC	250	150	[13]
		THF$—C_2H_5$	56,56*				
		$CH_3—(CH_2)_5—CH_3$	56,6				
92	F $—CH{=}CH—CH{=}O$	$CH_3(CH_2)_5—CH_3$	12345,6	$NiO+MoS_2$	307	100	[53]
				Ni	>300	100	[53]
93	F $—CHOH—CH_3$	$CH_3—(CH_2)_4—CH_3$	1235,6	$NiO+MoS_2$	340	100	[53]
94	F $—H$	$CH_3—(CH_2)_2—CH_3$	135,6	Ni	>300	—	—
95	THF $—H$	$CH_3—(CH_2)_2—CH_3$	35,6	Ni	300	—	—

$u = -5.6$ [8], and the maximum of the broken line is found at $u/2 = -2.8$, i.e. lower than for furan. The value of E'_a for the hydrogenation of benzene is equal to E' for the hydrogenation of the C=C bond after subtracting $\frac{\sigma}{2} = 18$, or $E'_a = -20$, i.e. benzene is hydrogenated with greater difficulty than is furan, for which $E' = -11$, which agrees with experiment. For the mechanism of benzene ring hydrogenation see [56].

The system of bond energies Q [6, 7] at times differs from the experimental values of $\underline{u}$ (thus, for the heat of hydrogenating the carbonyl bond, $u = 14$ from Q by [6], and $u = 12$ by the experimental data in [57] instead of $u = 7.7$ in [8]; the heat of hydrogenating furan is 14.1 instead of the observed 11.4). We use the given system for the reason that on the whole it gives correct data, and also because the corrections in Q show mutual compensation to considerable degree [2, 4]. In a previous communication [58], making use of a former less accurate Q system, we came to the same qualitative conclusions as we do here, since the principles involved were identical. In view of the fact that the Q values are still insufficiently known, calculation gives only mutual positions, and not the absolute values of E'. It is essential that the obtaining of a whole collection of E' levels on the basis of only a few, although close to the thermochemical, bond energies of atoms with the catalyst agree with experiment, as is required by the multiplet theory.

For the hydrogenation of the benzene ring over nickel, $E' = -20$ proves to be lower than for the hydrogenolysis of the C−O bond, $E' = -16.8$. Table 2 confirms this (Nos. 87, 88, 38); however, exceptions also exist (for example, the hydrogenation of phenol to cyclohexanol), possibly associated with the influence of substituents; for this reason the problem requires additional study. The importance for catalysis of a more accurate experimental delineation of bond energy values, and especially not of the average, but of the individual values, can be seen from the above discussion.

In the absence of the latter we do not touch on the theory of the influence of substituents on hydrogenation selectivity in this paper. Experimental material reveals that here its own rules exist. Thus, we find that over nickel the hydrogenolysis of the C−O bond in the tetrahydrofuran cycle proceeds with greater difficulty than it does in an open chain (see Nos. 33, 55, 57, 87 and 88, Table 2). It is possible that this is associated with the difficulty of free rotation in the multiplet complex.

In conclusion we will examine the question of the influence shown by the catalyst nature. Here the question arises, why does the C=C(f) bond in furan show more difficult hydrogenation over copper than does hydrogenolysis of the C−O(f) bond [9], while in the case of nickel, as we saw, just the opposite is true ? In other words, it is necessary to find the conditions under which the following inequalities are fulfilled

$$E'_{\mathrm{C=C(f),\,Ni}} > E'_{\mathrm{C-C(f),\,Ni}}, \tag{10}$$

$$E'_{\mathrm{C-O(f),\,Cu}} > E'_{\mathrm{C=C(f),\,Cu}}, \tag{11}$$

where, after what has been said above, the designations are self-evident. Substituting here the values of E' from Equation (2) and adding the obtained inequalities, we find:

$$-Q_{\mathrm{C=C(f)}} - Q_{\mathrm{H-H}} + 2Q_{\mathrm{Cf\,Ni}} + Q_{\mathrm{HNi}} > -Q_{\mathrm{C-O(f)}} - Q_{\mathrm{H-H}} + Q_{\mathrm{Cf\,Ni}} + 2Q_{\mathrm{HNi}}. \tag{12}$$

$$\begin{array}{r} -Q_{\mathrm{C-O(f)}} - Q_{\mathrm{H-H}} + Q_{\mathrm{Cf\,Cu}} + Q_{\mathrm{Of\,Cu}} + 2Q_{\mathrm{HCu}} > -Q_{\mathrm{C=C(f)}} - Q_{\mathrm{H-H}} + \\ + 2Q_{\mathrm{Cf\,Cu}} + 2Q_{\mathrm{HCu}} \\ \hline \end{array} \tag{13}$$

$$Q_{\mathrm{Cf\,Ni}} + Q_{\mathrm{Of\,Cu}} > Q_{\mathrm{Of\,Ni}} + Q_{\mathrm{Cf\,Cu}} \tag{14}$$

From which the sought condition:

$$Q_{\mathrm{Of\,Cu}} - Q_{\mathrm{Cf\,Cu}} > Q_{\mathrm{Of\,Ni}} - Q_{\mathrm{Cf\,Ni}} \tag{15}$$

An attempt to evaluate the bond energies $Q_{C_f Ni}$ and $Q_{C_f Cu}$ could be made. In catalysis Q_{O-Ni} = = 48.5, and thermochemical Q_{O-Ni} = 59; if the difference (10.5) is also the same for Cu, then catalytic Q_{O-Cu} = 47 − 10.5 = 36.5 kcal. From the above discussion, in the hydrogenation of furan the energy of the intermediate doublet complex is lowered by $\frac{\sigma}{2}$ = 8, or by 4 kcal. for 1 Ni atom. Then Q_{O_f-Ni} = = Q_{O-Ni} + 4 = 52.5, Q_{C_f-Ni} = 19 + 4 = 23 and Q_{O_f-Cu} = 36.5 + 4 = 50.5. Substituting these data in (15), we find that $Q_{C_f Cu}$ < 11 kcal. As a result, the bond energy of a furan carbon with copper should be considerably less than with nickel.

This proves to be in accord with the fact that copper, in contrast to nickel, fails to catalyze the hydrogenation of benzene for the specific reason that a very low bond energy is shown by the combination of benzene carbon atoms with Cu [3]. It is for this same reason that copper fails to form carbides.

From the multiplet theory it follows that due to variation in q on different catalysts the reaction sequences can prove to be different. This explains, together with what has been said above, also the fact that on a Pt-Fe catalyst [59] Reactions 1 and 2 change places, while Reaction 3 now fails to precede hydrogenolysis of the ether linkage in the furan ring.

The results of the present study show the fruitfulness of applying the multiplet theory to the hydrogenation of furan compounds.

SUMMARY

1. A definite sequence of reactions for the hydrogenation of furan compounds on nickel was derived with the aid of the multiplet theory of catalysis (Table 1). This rule was verified on approximately 100 transformations, known from experiment, in which connection it was confirmed almost without exception (Table 2).
2. It was explained why the furan ring is hydrogenated more easily than is the benzene ring.
3. It was shown that the theory permits expecting a different sequence of reactions on different catalysts.
4. It was explained why the sequence of reactions with hydrogen for the bonds in the furan ring is different on copper than on nickel.

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HYDROXYDIHYDROFURANS

V. BASIC PROPERTIES OF 5, 5-DIMETHYL-2-TERT-BUTYL-4-PHENYL-2-HYDROXY-2, 5-DIHYDROFURAN

E. D. Venus-Danilova, A. Fabritsy and A. N. Orlova

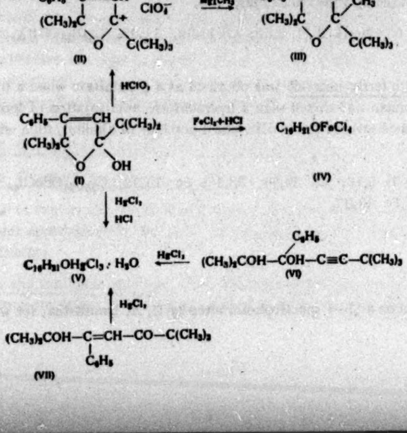
In the previous communication [1] it was shown that the basic properties (ability to give salts with acids) of 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran are determined, not by the ability of this substance to give oxonium compounds, but by the formation of the carbonium ion; and some new anhydrous salts of the 2-hydroxydihydrofuran were described – the perchlorate, picrate and also its complex salts with mercuric chloride and ferric chloride.

In this paper we describe the basic properties of another substance from the group of 2-hydroxy-2,5-dihydrofurans, and specifically 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran (I), which molecule differs from our earlier studied 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran only in that an aliphatic (tert-butyl) radical is found instead of an aromatic radical (phenyl) in the 2 position of the 2-hydroxydihydrofuran ring. The presence of this radical favored a reduction in the basic properties of the substance. It is known [2] that the hydrochloride of a 2-hydroxy-2,5-dihydrofuran with a tert-butyl radical is extremely unstable and shows easy hydrolysis, while the chloroplatinate and aurate are stable.

We were able to obtain for 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran a stable anhydrous perchlorate (II), which when reacted with methylmagnesium iodide gave 2,2,5-trimethyl-5-tert-butyl-3-phenyl-2,5-dihydrofuran (III). The complex salts of this hydroxydihydrofuran with ferric chloride (IV) and with mercuric chloride (V) were synthesized.

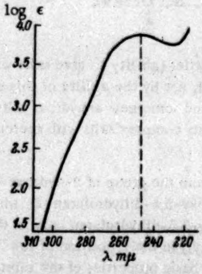
A complex salt with mercuric chloride is also formed when the unsymmetrical dimethyl-phenyl-tert-butylethynylethylene glycol (VI) and the ethylene γ-ketoalcohol – 2,6,6-trimethyl-3-phenyl-3-hepten-2-ol-5-one (VII) – are reacted with mercuric chloride in alcohol solution under heating, but in lower yield.

The studied transformations can be depicted schematically.



A reduction in the basic properties shown by substituted 2-hydroxy-2,5-dihydrofurans when an aryl radical in in position 2 is replaced by an alkyl is in accord with the phenomena observed in the benzopyrylium series. The alkyl-substituted chromenols are weak bases and also only form stable complex salts, and not the simple salts (with the exception of perchlorates); the introduction of aryl radicals sharply raises the basic properties of these compounds [3].

It is possible that this change in basicity is responsible for the reduction in color of the 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran cation (in the complex salts with ferric chloride the anion is colored) when compared with the yellow color of the cation of 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran salts. This is supported by literature data, since it is known that the perchlorate of 2,4,6-trimethylpyrylium is colorless, while replacement of the methyl group in the 4 position by phenyl results in the appearance of a light yellow color [4]; the salts of 2,4,6-triphenylpyrylium are colored bright yellow [5].



The reaction between the perchlorate of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran and methylmagnesium iodide, despite the lower basicity shown by this hydroxydihydrofuran, proceeds in exactly the same manner as for the perchlorate of 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran [1] and leads to a single product – 2,5,5-trimethyl-2-tert-butyl-4-phenyl-2,5-dihydrofuran (III), completely devoid of basic properties. The presence of pinacolin among the oxidation products of (III) shows that in this case also there was addition of a methyl group in the 2 position of the 2-hydroxydihydrofuran ring, similar to our earlier obtained 2-hydroxy-2,5-dihydrofuran with a phenyl radical [1], and also for benzopyrylium salts with a substituent in the 4 position [6].

The absorption curve for 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran (λ 246-248 mμ, ϵ 8400.9) (figure) in the ultraviolet region of the spectrum * almost coincides with the absorption curve for 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran, given in the previous communication [1] (figure).

EXPERIMENTAL

Synthesis of Simple and Complex Salts of 5,5-Dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran

The perchlorate was obtained by adding an excess of perchloric acid in ether solution to an ether solution of 6 g of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran (b. p. 135° at 3 mm, n_D^{20} 1.5234). A colorless crystalline precipitate separated immediately, which after washing with ether and drying in the air melted with decomposition at 175-176°. Yield 64%.

Found %: C 58.21, 58.29; H 6.71, 6.58; Cl 11.09, 11.03. $C_{16}H_{21}OClO_4$. Calculated %: C 58.45; H 6.39; Cl 10.81.

The complex salt with ferric chloride was obtained as a precipitate when a hydrochloric acid solution of the 2-hydroxy-2,5-dihydrofuran was mixed with a hydrochloric acid solution of ferric chloride. The brownish-yellow precipitate was washed several times with small portions of alcohol, then with ether and air dried, after which it had m. p. 121°.

Found %: C 44.76; H 5.16; Cl 32.83, 33.17; Fe 13.02. $C_{16}H_{21}OFeCl_4$. Calculated %: C 44.98; H 4.92; Cl 33.27; Fe 13.07.

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* The spectrum was taken on a SF-4 spectrophotometer by U. A. Dranitsina, for which we wish to thank her.

Complex salt with mercuric chloride. When a solution of 1.2 g of the 2-hydroxy-2,5-dihydrofuran in 10 ml of 96% ethyl alcohol was mixed with a solution of 1.4 g of mercuric chloride in 8 ml of alcohol we failed to observe any change in the course of a day and then when heated for 2 hours at alcohol boil. The addition of 8 drops of concentrated hydrochloric acid immediately gave a white crystalline precipitate, which after washing with a small amount of alcohol and drying had m. p. 164-165° (decomp.). Yield 2 g (82%).

Found %: C 34.40; H 4.36; Cl 18.74; Hg 36.48. $C_{16}H_{21}OHgCl_3 \cdot H_2O$. Calculated %: C 34.63; H 4.15; Cl 19.22; Hg 36.21.

Preparation of 2,5,5-Trimethyl-2-tert-butyl-4-phenyl-2,5-dihydrofuran

To an ether solution of methylmagnesium iodide, obtained from 1.1 g of magnesium and 7 g of methyl iodide (a 3.5-fold amount with respect to the perchlorate), was added 4.5 g of the dry perchlorate in 6 portions and in 40 minutes. During perchlorate addition the appearance of a bright pink color was observed, which gradually disappeared in 2-3 minutes. After all of the perchlorate had been added the reaction mass was heated for 10 minutes under weak ether boil, then cooled to room temperature, poured on ice, decomposed with aqueous ammonium chloride solution, and extracted with ether. After drying and ether removal the residue in an amount of 2.5 g (76%) was vacuum distilled.

B. p. 126-127° (5 mm), d_4^{20} 0.9561, n_D^{20} 1.5164, MR_D 77.12; calc. 76.08.

Found %: C 83.41, 83.37; H 10.00, 10.10. M 251. $C_{17}H_{24}O$. Calculated %: C 83.61; H 9.83. M 244.

From its analysis the substance is 2,5,5-trimethyl-2-tert-butyl-4-phenyl-2,5-dihydrofuran.

Oxidation of the dihydrofuran. For 2 g of the dihydrofuran was taken 4.3 g of potassium permanganate (calculated on the basis of 10 moles of oxidizing agent for 3 moles of the dihydrofuran). A part of the oxidizing agent was added in aqueous solution (200 ml of 1.5% $KMnO_4$), while the remainder was added as a dry, finely divided powder. The oxidation was run under vigorous stirring and at first proceeded very slowly, so finally we heated the reaction mass at 35-40°. After all of the oxidizing agent had been added the mixture was heated an additional hour at 40° and then 1 g of potash was added. After 2 days the manganese dioxide precipitate was filtered from the colorless solution, after which the solution was extracted with ether. The small amount of residue, obtained after distilling off the ether, was distilled through an efficient dephlegmator at 95-105° and gave a 2,4-dinitrophenylhydrazone (m. p. 124-125°) and a semicarbazone (m. p. 156-157°), both corresponding to pinacolin (mixed melting point). The residue from the distillation was 0.5 g of a liquid (n_D^{20} 1.5151), apparently being the starting dihydrofuran.

The water solution, remaining after ether extraction of the neutral products, was heated on the water bath. Several drops of a volatile substance distilled at 50-60°, giving a 2,4-dinitrophenylhydrazone with m. p. 125°, corresponding to acetone (mixed melting point).

The aqueous solution of organic acids, obtained after decomposing their salts and removing the benzoic acid with m. p. 119-120° (confirmed by distillation and mixed melting point), was divided into two portions; traces of formic acid were found in one portion (mercuric chloride, ammoniacal solution of silver oxide), while the other portion gave a qualitative test with phenylhydrazine hydrochloride for traces of benzoylformic acid [7]. Then the last portions of benzoic acid were extracted from both portions with ether. Here we were unable to find any methyl-tert-butylglycolic acid, since it easily gives pinacolin when oxidized [8].

Reaction of Mercuric Chloride with the Unsymmetrical Dimethyl-phenyl-tert-butylethynylethylene Glycol and with 2,6,6-Trimethyl-3-phenyl-3-hepten-2-ol-5-one

Several experiments were run on the reaction of mercuric chloride with the acetylene glycol and with the ethylene γ-ketoalcohol under approximately the same conditions, in which connection similar results were obtained in all of the experiments.

Experiment 1. Glycol and mercuric chloride. The solutions of 1.8 g of the glycol (m. p. 65-66°) in 10 ml of 95% alcohol and 2 g of mercuric chloride in 10 g of alcohol (1 mole of glycol for 1 mole of mercuric chloride) were mixed at room temperature. For 10-15 minutes a change failed to be observed, but after this the solution gradually began to acquire a pink color. Coarse aggregates of colorless crystals began to appear on the surface of the liquid, which fell to the bottom, forming a white precipitate. When stirred and heated slightly the solution acquired a pink-lilac color, while the precipitate gradually disappeared. After heating for 1 hour under weak alcohol boil the reaction mass was let stand a day at room temperature, after which the deposited light lilac precipitate was filtered from the pink-violet solution, washed twice with small amounts of alcohol (partial solution), and air dried. The substance is difficultly soluble in cold alcohol, quite readily soluble in hot alcohol, and very difficultly soluble in ether and benzene; it melts at 166° with decomposition, and begins to darken and sinter at 160°. When mixed with the substance, obtained in the treatment of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran with mercuric chloride in the presence of hydrochloric acid, it fails to lower the melting point. The yield of substance was 2.2 g (55%, calculated on the basis of the complex $C_{16}H_{21}OHgCl_3 \cdot H_2O$).

The analysis for mercury and chlorine gives unsatisfactory results (more mercury, less chlorine). Recrystallization from alcohol fails to aid purification. However, after washing with benzene the violet color of the crystals disappears, and satisfactory analysis results are obtained.

Found %: Hg 36.35; Cl 18.91. $C_{16}H_{21}OHgCl_3 \cdot H_2O$. Calculated %: Hg 36.21; Cl 19.22.

After removal of the crystalline substance from the violet colored filtrate the alcohol was removed by distillation under slight vacuum. To the violet colored residue was added 5 ml of water, and then an extraction with warm benzene was made. Removal of the benzene by evaporation left a residue of small violet-crimson crystals, which showed deliquescence in the air and lost their color here, which crystals were not studied further because of their small amount. From the ether extract, made after the benzene extract, was obtained 1-2 drops of a black viscid mass.

Experiment 2. Glycol and mercuric chloride in the presence of hydrochloric acid. To a clear solution of 1 g of the glycol and 1.2 g of mercuric chloride (1 : 1) in 20 ml of ethyl alcohol was added at room temperature 6 drops of concentrated hydrochloric acid. Immediately a precipitate formed, while the solution acquired a pink-violet color. After heating for 1.5 hours under weak alcohol boil there was obtained 1.3 g (64%) of a light lilac colored substance, which after washing with benzene melted at 165° (decomp.) and failed to show a melting point depression when mixed with the substance obtained in Experiment 1.

Experiment 3. Ethylene γ-ketoalcohol and mercuric chloride. A solution of 1.4 g of 2,6,6-trimethyl-3-phenyl-3-hepten-2-ol-5-one (b. p. 134-135° at 4 mm, n_D^{20} 1.5260) and 1.7 g of mercuric chloride (1 : 1) in 20 ml of ethyl alcohol was prepared. At room temperature there was neither a change in color nor the separation of a precipitate. The addition of 8 drops of concentrated hydrochloric acid gave a small amount of precipitate. Then the solution was heated for 2 hours under weak alcohol boil. Cooling of the alcohol solution gave 0.8 g (28.2%) of crystalline precipitate with m. p. 164° (decomp.), corresponding to the complex salt of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran, while from the benzene extract was obtained 2.6 g of viscous purple-black liquid, containing both chlorine and mercury, and apparently being the mercuration product of the unsaturated γ-ketoalcohol. The residue was not subjected to closer study.

SUMMARY

1. In studying the reaction of mercuric chloride with the unsymmetrical dimethyl-phenyl-tert-butyl-ethynylethylene glycol and the isomeric 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran and 2,6,6-trimethyl-3-phenyl-3-hepten-2-ol-5-one it was elucidated that all of these substances form one and the same compound, corresponding to the complex mercury salt of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran.

2. It was confirmed that the basic properties of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran are determined by the formation of the carbonium ion and that this substance, similar to the earlier studied 5,5-dimethyl-2,4-diphenyl-2-hydroxy-2,5-dihydrofuran, gives dihydrofurylium salts with acids.

3. Anhydrous salts of 5,5-dimethyl-2-tert-butyl-4-phenyl-2-hydroxy-2,5-dihydrofuran with ferric chloride and with perchloric acid were obtained, and also the reaction product of the perchlorate of this 2-hydroxy-2,5-dihydrofuran with methylmagnesium iodide – 2,5,5-trimethyl-2-tert-butyl-4-phenyl-2,5-dihydrofuran.

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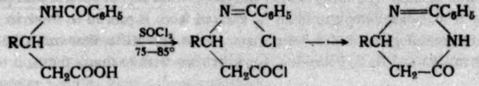
SYNTHESES IN THE PYRIMIDINE SERIES

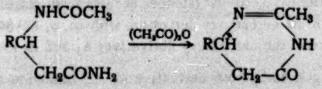
II. TRANSFORMATION OF DIASTEREOISOMERIC γ-ETHYL-β-AMINOCAPRYLIC ACIDS INTO SUBSTITUTED TETRA- AND HEXAHYDROPYRIMIDINES

V. M. Rodionov* and V. K. Zvorykina

In our previous studies we mentioned the great tendency shown by N-acylated derivatives of β-amino acids to form substituted pyrimidines, and outlined methods for the synthesis of 2,4-dialkyl (and arylalkyl)-6-oxotetrahydropyrimidines, and also of 4-alkyl (aryl)-2,6-dioxohexahydropyrimidines [1]. It was shown that the N-benzoyl derivatives of β-amino acids are converted in good yield into 2-phenyl-6-oxotetrahydropyrimidines by treating them with thionyl chloride at 75-85° and subsequent saturation with ammonia:



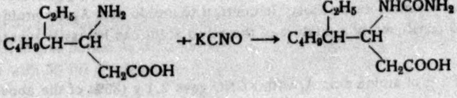
A more convenient method for the preparation of 2-methyl-6-oxotetrahydropyrimidines proved to be a different approach – ring closure of the amides of the acetyl derivatives with acetic anhydride:



We used these reactions to synthesize anew the members of the aliphatic β-amino acid series with a radical of iso-structure, and specifically – the two diastereoisomeric γ-ethyl-β-aminocaprylic acids, provisionally designated as A_1 and A_2 [2].

From these two isomers we obtained the corresponding 2-phenyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidines and 2-methyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidines. In addition, from both isomers we synthesized the β-ureido acids, which were then converted under the conditions described by Rodionov and Vyazkova [3] into 4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidines; here the intermediate γ-ethyl-β-ureidocaprylic acids were obtained by the following three methods.

1) The heating of amino acids with KCNO [4]:



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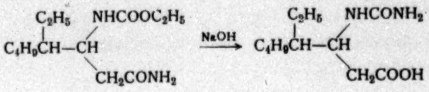
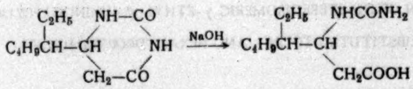
* Deceased.

2) The heating of the amides of N-carbethoxy derivatives of γ-ethyl-β-aminocaprylic acids with alkali [5]:



3) The saponification of 4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidines:



When compared with the derivatives of other β-amino acids the melting points of the γ-ethyl-β-ureidocaprylic acids and of the substituted 2,6-dioxohexahydropyrimidines obtained from them proved to be somewhat unusual. Usually the 4-alkyl (aryl)-2,6-dioxohexahydropyrimidines melt 30-50° higher than do the starting ureido acids. In the case of isomer A_1 the ureido acid melts only 11° higher than the corresponding pyrimidine, while for isomer A_2 the ureido acid melts even 23° lower than does the substituted pyrimidine derived from it.

It is also interesting to mention that of the two stereoisomers of γ-ethyl-β-ureidocaprylic acid only the A_2 isomer proved capable of showing bacteriostatic activity toward mycobacteria and pathogenic fungi, while the 4-(1'-ethylpentyl)-6-oxohexahydropyrimidine A_2 derived from it proved to show in vitro activity against the virus group. The microbiological studies were made in the Scientific-Research Chemical-Pharmaceutical Institute by S. N. Milovanova and N. S. Butyrkina, for which we wish to thank them.

EXPERIMENTAL

Preparation of amides of isomeric N-carbethoxy-γ-ethyl-β-aminocaprylic acids A_1 and A_2. The carbethoxy derivatives were obtained in the usual manner. From 12 g of amino acid A_1 was obtained 12.2 g (74%) of the carbethoxy derivative with m. p. 60-61° (slender needles from petroleum ether). From 2.5 g of amino acid A_2 was obtained 2.35 g (70%) of the carbethoxy derivative with m. p. 63-64° (needles from a mixture of ethyl and petroleum ethers). The mixture of the carbethoxy derivatives A_1 and A_2 melts at 50-53°.

To obtain the amide 12 g of carbethoxy derivative A_1 was heated at 40° for 3 hours with 5 ml of $SOCl_2$; the excess $SOCl_2$ was vacuum distilled, 500 ml of ether was added to the residue, and the solution under cooling was saturated with ammonia. There was obtained 8.15 g (68%) of the amide with m. p. 146° (colorless slender needles from water). Under similar conditions from 1.5 g of carbethoxy derivative A_2 was obtained 1.15 g (70.6%) of the amide with m. p. 144° (tiny colorless needles from water). The mixture of amides A_1 and A_2 melts at 132-133°.

Found for isomer A_1 %: C 60.64, 60.50; H 10.15, 10.07; N 10.89, 10.86. Found for isomer A_2 %: C 60.78, 60.64; H 10.08, 10.20; N 10.87, 10.96. $C_{13}H_{26}O_3N_2$. Calculated %: C 60.46; H 10.07; N 10.85.

Preparation of isomeric γ-ethyl-β-ureidocaprylic acids A_1 and A_2. a) One gram of the amide of carbethoxy derivative A_1 was boiled with 20 ml of 10% NaOH solution until the precipitate dissolved. Acidification gave 0.75 g (86%) of ureido acid A_1 with m. p. 142° (flat colorless needles from water).

Under the same conditions 1 g of the amide of carbethoxy derivative A_2 gave 0.85 g of ureido acid A_2 with m. p. 169° (colorless prisms from alcohol). In contrast to ureido acid A_1 the ureido acid A_2 is very difficultly soluble in hot water, and consequently a mixture of these two acids can be easily separated by recrystallization from hot water.

b) The heating of 2 g of amino acid A_1 with KCNO gave 2.1 g (85%) of the above described ureido acid A_1 with m. p. 141-142°.

From 20 g of amino acid A_2 hydrochloride (with the A_1 isomer as impurity) under heating with 400 ml of water, 4 g of NaOH and 8 g of KCNO was obtained a mixture of ureido acids A_1 and A_2 with m. p. 156-158°. Boiling of this mixture with 100 ml of water gave the ureido acid A_1 from solution (1.12 g, 6%) with m. p. 140°. The residue failing to dissolve was recrystallized from alcohol. There was obtained 15.2 g (76%) of ureido acid A_2 with m. p. 168°. Both ureido acids are readily soluble in Na_2CO_3, but insoluble in $NaHCO_3$. Under prolonged heating with 5% NaOH they are partically converted into the starting amino acids.

Found for isomer A_1%: C 57.34, 57.23; H 9.58, 9.45; N 11.91, 12.07. Found for isomer A_2%: C 57.65, 57.76; H 9.87, 9.91; N 11.89, 11.86. $C_{11}H_{22}O_3N_2$. Calculated %: C 57.39; H 9.57; N 12.17.

Preparation of isomeric 4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidines A_1 and A_2. A solution of 0.5 g of ureido acid A_1 in 50 ml of 12% HCl was boiled for 3 hours. On cooling there was deposited 0.31 g (67%) of pyrimidine A_1 with m. p. 152° (slender colorless needles from water). Under the same conditions 5 g of ureido acid A_2 gave 3.9 g (80%) of pyrimidine A_2 with m. p. 145-146° (thin slender platelets from water). The mixture of both isomers melts at 134-138°.

Found for isomer A_1%: C 61.98, 62.12; H 9.37, 9.50; N 13.28, 13.44. Found for isomer A_2%: C 62.06, 62.06; H 9.44, 9.30; N 13.37, 13.40. $C_{11}H_{20}O_2N_2$. Calculated %: C 62.26; H 9.43; N 13.21.

Both of the 4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidine isomers dissolve in cold 10% NaOH and when acidified are deposited in unchanged form. When boiled with 5-10% NaOH solution for 0.5-1 hour they show cleavage of the pyrimidine ring, and on acidification the corresponding ureido acids precipitate.

Preparation of isomeric 2-phenyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidines A_1 and A_2. A mixture of 5 g of the benzoyl derivative of amino acid A_1 with m. p. 132° [2] and 3.75 ml of $SOCl_2$ was heated for about 3 hours at 75-80°. The excess $SOCl_2$ was vacuum distilled, 500 ml of ether was added to the residue, and the solution under cooling was saturated with ammonia. The yield of pyrimidine A_1 with m. p. 125° was 2.1 g (44.8%) (thin slender needles from aqueous alcohol).

Under the same conditions 5 g of the A_2 benzoyl derivative with m. p. 121° [2] gave 2.9 g (62%) of the pyrimidine with m. p. 123° (slender needles from aqueous alcohol).

Found for isomer A_1%: C 75.26, 75.07; H 8.57, 8.69; N 10.16, 10.08. Found for isomer A_2%: C 74.79, 74.91; H 9.08, 9.02; N 10.25, 10.49. $C_{17}H_{24}ON_2$. Calculated %: C 75.00; H 8.82; N 10.29.

Preparation of isomeric 2-methyl-4-(1'ethylpentyl)-6-oxotetrahydropyrimidines A_1 and A_2. From 10 g of amino acid A_1 in 10% NaOH solution under $(CH_3CO)_2O$ addition was obtained 10.6 g (81.3%) of the A_1 acetyl derivative with m. p. 118° (colorless needles from water). From 5 g of amino acid A_2 under the same conditions was obtained 4.35 g (78.8%) of the A_2 acetyl derivative with m. p. 117° (thin colorless needles from water). The mixture of isomers A_1 and A_2 melts at 98-101°.

Found for isomer A_1%: N 6.05, 6.09. Found for isomer A_2%: N 6.24, 6.28. $C_{12}H_{23}O_3N$. Calculated %: N 6.11.

The corresponding amides were obtained by heating the acetyl derivatives with the theoretical amount of $SOCl_2$ at 40-45° and subsequent saturation of the ether solutions with NH_3. From 75 g of the A_1 acetyl derivative was obtained 6.7 g (89.3%) of the A_1 amide with m. p. 195° (slender colorless needles from alcohol). From 4 g of the A_2 acetyl derivative was obtained 3.1 g (77.6%) of the A_2 amide with m. p. 175° (elongated platelets from alcohol).

Found for isomer A_1%: N 12.45, 12.40. Found for isomer A_2%: N 12.40, 12.20. $C_{12}H_{24}O_2N_2$. Calculated %: N 12.28.

To obtain 2-methyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidine a mixture of 1.5 g of amide A_1 and 30 ml of acetic anhydride was boiled for 4 hours; then the excess anhydride was removed by distillation, and the residue was treated with 50 ml of water; the solution was boiled for 20 minutes and extracted with ether.

There was isolated 1,05 g (76%) of pyrimidine A_1 with m. p. 92° (slender needles from aqueous alcohol). Pyrimidine A_2 was obtained under similar conditions; m. p. 86-87° (flat needles from ether). Yield about 70%.

Found for isomer A_1 %: C 68.80; H 10.88; N 13.40, 13.30. Found for isomer A_2 %: C 68.22, 68.42; H 10.59, 10.30; N 13.29, 13.39. $C_{12}H_{22}ON_2$. Calculated %: C 68.57; H 10.48; N 13.33.

SUMMARY

Three methods were used to obtain the isomeric γ-ethyl-β-ureidocaprylic acids, and, on their closure, the 4-(1'-ethylpentyl)-2,6-dioxohexahydropyrimidines, from the two diastereoisomeric γ-ethyl-β-aminocaprylic acids.

Treatment of the benzoyl derivatives of the diastereoisomeric γ-ethyl-β-aminocaprylic acids, first with $SOCl_2$, and then with NH_3, gave the isomeric 2-phenyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidines. Heating of the diastereoisomeric γ-ethyl-β-(N-acetylamino)caprylic acids with acetic anhydride gave the isomeric 2-methyl-4-(1'-ethylpentyl)-6-oxotetrahydropyrimidines.

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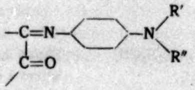
AZOMETHINE DYES FROM OXINDOLE DERIVATIVES. I.

M. S. Kisteneva

In recent years the azomethine dyes — derivatives of various ketomethylene compounds with a substituted p-diamine radical (I) — have assumed great practical value, since they are the substances that form the image in the development of colored films [1].

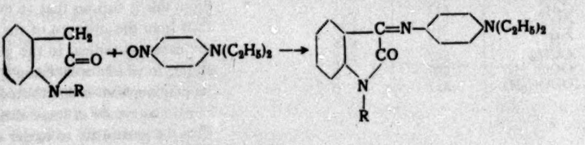


The color (zone and shape of the absorption curve) of such azomethine dyes, giving a colored image, is essentially determined by the structure of the carbonyl-containing radical. The entrance of substituents into this radical can cause considerable shifting of all of the absorption bands of dyes [2], while at the same time the presence of various groupings in the diamine radical in most cases fails to show much influence on the position of the absorption maximum.

Among such azomethines the dyes containing the oxindole radical have been left almost completely unstudied. Only individual 3-p-aminoanils of isatins have been described in the literature [3-5]. In some patents [6] oxindole derivatives are postulated as being the purple component of dyestuffs. However, there fail to be any data either on the position of the absorption maxima of azomethine dyes from oxindole derivatives, or on the relationship between their color and structure.

In this work we studied the influence shown by the presence of various substituting groups on the nitrogen atom of the hetero radical on the color of azomethine dyes belonging to the class of oxindole derivatives (β-dialkylaminoanils).

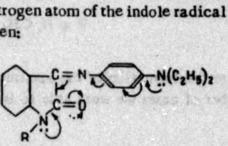
We synthesized a number of oxindole derivatives, and from them by treatment with p-nitrosodiethylaniline in alcohol solution in the presence of piperidine traces we obtained the corresponding azomethine dyes:



R = H, CH_3, C_2H_5, C_6H_5, $COCH_3$, OH, OCH_3, $OCOCH_3$ and $OCOC_6H_5$.

Here the formation of the azomethine dyes was usually accompanied by secondary processes (see [7]), and in a number of cases we were able to isolate the pure substances only by resorting to the chromatographic method.

A study of the absorption spectra of the synthesized dyes in alcohol solutions (Figs. 1 and 2) revealed that they have one absorption band and their color as a function of the presence of substituents changes within fairly wide limits. As can be seen from the data in Table 1, replacement of a hydrogen in the nitrogen atom of the oxindole radical of the examined dyes by an alkyl group results in slight hypsochromic shift, while in the transition to the N-phenyl and especially the N-acetyl derivative a considerable shifting of the absorption maximum toward the long wavelength portion of the spectrum is observed. The presence of a hydroxy group in position 1 also results in noticeable bathochromic effect, which decreases when the hydroxy group is methylated and disappears completely when it is acylated. These rules become more intelligible when the structures of the indicated dyes are examined. A comparison of the positions of the absorption spectra in different solvents of the simplest dye of this group (Table 2) reveals that its color deepens with increase in polarity of the medium. From this it follows that in ethyl alcohol the electron shift from the nitrogen of the diethylamino group to the carbonyl radical in the given dye is comparatively slight, in which connection the electron density in its chromophore is distributed nonuniformly [8]. The small magnitude of these shifts is evidently associated with the possibility of easier withdrawal of an electron from the nitrogen atom of the indole radical by the carbonyl oxygen:



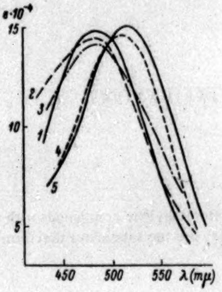


Figure 1. Absorption curves of (II) dyes in C_2H_5OH, where R equals: 1) H, 2) CH_3, 3) C_2H_5, 4) C_6H_5, 5) $COCH_3$.

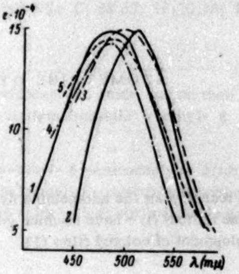
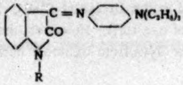


Figure 2. Absorption curves of (II) dyes in C_2H_5OH, where R equals: 1) H, 2) OH, 3) OCH_3, 4) $OCOCH_3$, 5) $OCOC_6H_5$.

TABLE 1.

Position of the Absorption Maxima of 3-p-Diethylaminoanils of Isatins in Alcohol Solutions



R	Absorption maximum (in mμ)	Shift (in mμ)
H	487	—
CH_3	484	—3
C_2H_5 . . .	486	—1
C_6H_5 . . .	511	+24
CH_3CO . .	516	+29
OH	512	+25
OCH_3 . . .	502	+15
$OCOCH_3$.	487	0
$OCOC_6H_5$.	487	0

TABLE 2

Solvent	Absorption maximum of 3-p-diethylaminoanilisatin in solution (in mμ)
Benzene	480
Ethanol	485
Methanol	488

The introduction in position 1 of an electronegative group, which partially attracts an electron away from the nitrogen of the indole radical, will result in a weakening of the electron shifts from this atom toward the carbonyl oxygen. In connection with this the electron shifts from the diethylamino group along the conjugated chain show increase and the electron density distribution in the chromophore becomes more uniform, which should lead to a deepening of the dye color.

On the other hand, the introduction of an electropositive group, for example, an alkyl on the nitrogen atom, or its entrance into a negative radical (for example, alkylation of an OH group) should increase the electron shifts from the nitrogen atom of the hetero radical to the carbonyl oxygen. In association with this the uniformity of electron density distribution in the chromophore should decrease and the position of the absorption maximum of the dye is shifted toward the short wavelength region.

The relationship established by us of the influence shown by substituting groups on the color of isatin β-dialkylaminoanils supports these considerations. Not fully understood is the sharp rise in color observed in the acylation of the hydroxy group in 1-hydroxy-3-p-diethylaminoanilisatin. It is possible that this phenomenon is associated with electrostatic interaction of the closely situated carbonyl oxygen atoms of the acyloxy group and the oxindole radical, which leads to a polarization reduction in the main chromophore of the dye.

EXPERIMENTAL

I. Synthesis of oxindole derivatives. Oxindole was obtained by a slight modification of the Curtius and Thun method [9]. Ten grams of the isatin β-hydrazone [9] was very carefully melted in a 50 ml Claisen flask at 40-50 mm pressure (without sucking in air); here intense nitrogen evolution occurred with simultaneous sublimation of the product. After foaming had stopped the reaction mass was distilled at the same pressure. The fraction with b. p. 200-215° was collected. Yield 4.5-6 g (55-75%). Under rapid heating of the hydrazone the reaction proceeded vigorously and was accompanied by strong sublimation and tarring of the product.

When equal weight amounts (1: 1.25 mole) of chloroacetanilide and aluminum chloride were heated at 225° (according to Stolle [4]) we obtained only traces of oxindole. When the amount of aluminum chloride was increased to 2.25 mole [10] the oxindole was obtained in satisfactory yield; however, slight overheating of the reaction mass results in strong tarring.

N-methyloxindole. A mixture of 9.18 g of N-methylchloroacetanilide and 9.18 g of aluminum chloride was heated at 170-175° for 3 hours until hydrogen chloride ceased to evolve. After cooling, to the mixture was added 35 g of ice and 10 ml of 10% hydrochloric acid. The resulting precipitate was filtered and recrystallized twice from water, with the addition of activated carbon and several drops of hydrochloric acid. Yield 5.4 g (63%). M. p. 87-88° (88° [4, 11]). A more contaminated product is obtained when the reaction is run at 180° (according to Stolle [4, 11]).

N-ethyloxindole. Obtained in a similar manner by heating a mixture of 5 g of N-ethylchloroacetanilide and 5 g of aluminum chloride at 150-155° (according to Stolle [11] 160°) for 5 hours. Yield 2.4 g. Lustrous needlelike crystals. M. p. 95-96° (97° [11-13]).

N-phenyloxindole. Obtained in the same manner by heating a mixture of 4.9 g of N-phenylchloroacetanilide with 4.9 g of aluminum chloride at 160-165° (from Stolle 160-180°) for 5 hours. Yield 4 g (95.5%), m. p. 116-117°. For purification the product was first crystallized from alcohol with the addition of activated carbon, and then from ligroin. Yield 2.76 g (66%). Lustrous colorless leaflets with m. p. 121° (121° [11]).

N-acetyloxindole [14]. A mixture of 4 g of oxindole and 3.5 ml of acetic anhydride was boiled in a flask under reflux for 5.5 hours. The crystals that separated on cooling were filtered and washed with alcohol. Yield 4.2 g (80%). M. p. 125°. Recrystallization from water (with carbon addition) gave 3.6 g of light colorless crystals with m. p. 127° (126° [14]).

N-hydroxyoxindole (1,2-dioxindole) [16]. Obtained by us from o-nitrotoluene through the o-nitrophenylpyrotartaric and o-nitrophenylacetic acids.

a) o-Nitrophenylpyrotartaric acid was obtained by the Di Carlo method [15] – the condensation of o-nitrotoluene with ethyl oxalate in the presence of sodium ethylate, with subsequent saponification of the ester obtained here. For purification the highly contaminated product obtained by this method was washed with a small amount of hot benzene, after which it was recrystallized from water with the addition of carbon. The yield of purified product with m. p. 119-120° (119-120° [15, 16]) was 40-48%.

b) o-Nitrophenylacetic acid [16] was obtained in 90% yield by the oxidation of o-nitrophenylpyrotartaric acid with hydrogen peroxide.

c) To a mixture of 9 g of o-nitrophenylacetic acid, 150 ml of water and 21.3 g of sulfuric acid (d 1.83) under mechanical stirring was gradually added at 28-34° (water cooling) 8 g of zinc dust. The mixture was stirred another 3 hours at room temperature and then let stand overnight. The precipitate was filtered, washed with water and stirred with 50 ml of 5% sodium hydroxide solution. The unreacted zinc dust was removed by filtration and the filtrate was acidified with hydrochloric acid until it showed acid to Congo. The resulting precipitate was filtered, washed with 20% acetic acid and water, and desiccator-dried. Yield 5 g (67%). Yellow powder with m. p. 188-190° (with decomp.). For purification the dioxindole was boiled with 50 ml of water, the hot solution was filtered and the undissolved product was recrystallized from 150 ml of water with the addition of carbon. The precipitate, depositing from the first solution portion, was filtered and recrystallized twice from water (with carbon). The total yield was 74% of the reaction product weight. Almost colorless needles or prisms with m. p. 196-197° (198-199° [15]).

The N-methoxy-, N-acetoxy- and N-benzoyloxyoxindoles were obtained by treating a soda solution of the dioxindole with dimethyl sulfate, acetic anhydride and benzoyl chloride, respectively [17].

II. Synthesis of azomethine dyes. To obtain the dyes 0.005 mole of oxindole or its derivative and 0.005 mole of p-nitrosodiethylaniline were dissolved in 10 ml of anhydrous ethyl alcohol, containing a trace of piperidine, and the solution was boiled on the water bath in a flask under reflux.

3-p-Diethylaminoanilisatin. From the reaction solution was distilled 5 ml of alcohol, and the next day the deposited precipitate was filtered, washed with 2 ml of alcohol, and dried in a desiccator. Yield 45%. M. p. about 170° (decomp.). For purification the dye was recrystallized 3 times from ethyl alcohol. Fine dark red glistening crystals (dipyramids), m. p. 193° (decomp.).

Found %: N 14.18, 14.15. $C_{18}H_{19}ON_3$. Calculated %: N 14.33.

1-Methyl-3-p-diethylaminoanilisatin. The precipitate separating from the reaction mass on cooling was filtered, washed with alcohol, and dried in a desiccator. Yield 59%, m. p. 160°. The dye was recrystallized three times from ethyl alcohol and finally purified by chromatography. For this 0.5 g of the dye was dissolved in 70 ml of a benzenechloroform mixture (1:1). The solution was filtered (at a rate of 1-2 drops per second) through a column (diameter 15 mm, height 400 mm) filled with activated aluminum oxide. The adsorbed dye was eluted with the same benzene-chloroform mixture (1:1); here a small amount of dark violet substance, strongly adsorbed on the aluminum oxide, was separated. The dye solution was evaporated to dryness in vacuo at room temperature and the residue again recrystallized from ethyl alcohol. Fine brick-red crystals, m. p. 165°.

Found %: N 13.58, 13.67. $C_{19}H_{21}ON_3$. Calculated %: N 13.67.

1-Ethyl-3-p-diethylaminoanilisatin. The alcohol was distilled from the reaction solution in vacuo. To the residue (heavy sirup) was added 12 ml of ether, which was then also removed by distillation. The viscous mass obtained here partially crystallized on long standing. When seeded with some of the dye crystals it was possible to induce crystallization without the ether treatment. The crystals were filtered, washed with ligroin, and recrystallized twice from ethyl alcohol. M. p. 112-114°. Yield 17%. For final purification the product was chromatographed on aluminum oxide (see above). The dye was eluted with benzene and after distilling off the solvent was recrystallized from alcohol. Reddish brown plates. M. p. 115°.

Found %: N 12.95. $C_{20}H_{23}ON_3$. Calculated %: N 13.08.

1-Phenyl-3-p-diethylaminoanilisatin. The precipitate separating from the reaction solution after cooling was filtered, washed with ether, and dried in a desiccator. Weight 1.5 g. M. p. about 180° (not sharp). For purification the product was heated with 10 ml of alcohol. The hot solution was filtered and the residue was recrystallized 3 times from ethyl alcohol. The first crystallization gave 0.5 g of alcohol-insoluble substance. The yield of dye was 36%. Dark red rectangular plates with m. p. 185°.

Found %: N 11.23, 11.28. $C_{24}H_{23}ON_3$. Calculated %: N 11.38.

1-Acetyl-3-p-diethylaminoanilisatin. The deposited precipitate was filtered and washed with alcohol. Yield 74%. M. p. about 175° (not sharp). For purification the dye was recrystallized twice from ethyl alcohol. Yield 39%. Coarse crystals with a greenish tinge or tiny golden red needles. M. p. 186-187° (with decomp.).

Found %: N 12.48, 12.53. $C_{20}H_{21}O_2N_3$. Calculated %: N 12.53.

1-Hydroxy-3-p-diethylaminoanilisatin. The reaction solution was evaporated in vacuo. The residual semifluid ductile mass, readily soluble in benzene, alcohol and ether, was heated with 25 ml of ligroin, and the slightly red ligroin solution was decanted; here the residue turned into a hard, friable mass. Weight 1.5 g. Decomposition temperature around 120°. The precipitate was extracted with 10 ml of boiling ligroin and then with 10 ml of benzene. The residue (1 g) was heated with 12 ml of ethyl alcohol; the hot solution was filtered and then evaporated in vacuo to a volume of 5-6 ml. The small amount of precipitate separating here was filtered and recrystallized once more from ethyl alcohol. Very fine, dark red crystals with m. p. 168° (with decomp.).

Found %: N 13.41. $C_{18}H_{19}O_2N_3$. Calculated %: N 13.56.

Evaporation of the alcohol mother liquors gave a tarry mass, which we were unable to purify by crystallization.

1-Methoxy-3-p-diethylaminoanilisatin. The dye, separating when the reaction solution was cooled, and also after partial evaporation of the latter, was washed with alcohol and dried. Yield 52%. The dye was recrystallized twice from ethyl alcohol. Dark brown glistening needles with m. p. 183-185° (with decomp.).

Found %: N 13.10. $C_{19}H_{21}O_2N_3$. Calculated %: N 13.00.

1-Acetoxy-3-p-diethylaminoanilisatin. From the reaction solution was distilled 5 ml of alcohol; the resulting precipitate was filtered, washed with a small amount of alcohol, and dried. Yield 35%. The dye was recrystallized 3 times from ethyl alcohol. Tiny glistening crystals with m. p. 175° (with decomp.).

Found %: N 11.80, 12.00. $C_{20}H_{21}O_3N_3$. Calculated %: N 11.96.

1-Benzoyl-3-p-diethylaminoanilisatin. The solvent was removed from the reaction solution as completely as possible in vacuo. The residue – a nearly black, solid glistening mass – was purified by chromatography on aluminum oxide in benzene solution. The washing was run successively with benzene, chloroform and methyl alcohol. The elution with benzene gave a small amount of red and yellow secondary substances. Recrystallization of the residue from the evaporation of the chloroform solution gave 0.05 g of fine brownish red crystals with m. p. 181°.

Found %: N 10.35. $C_{25}H_{23}O_2N_3$. Calculated %: N 10.14.

From the methanol solution was isolated 0.2 g of by-product, containing 6.94% N.

SUMMARY

1. A number of azomethine dyes were synthesized from oxindole derivatives – the 3-p-diethylaminoanils of isatins, containing various substituting groups on the nitrogen atom of the indole ring.

2. The absorption spectra of the obtained azomethine dyes in alcohol solution were studied in the visible region. It was established that in the character of their absorption spectra the investigated dyes lie close to each other, but that the position of the absorption maximum of their solutions shows considerable change depending on the presence of substituents in the oxindole radical.

3. It was shown that the presence of electronegative groups in position 1 results in considerable shifting of the absorption maximum of these compounds toward the long wavelength portion of the spectrum. A slight rise in color is observed when electropositive groups are introduced.

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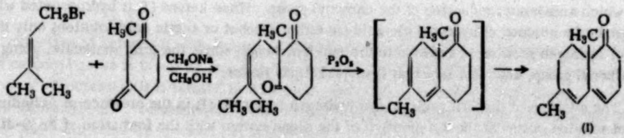
SYNTHESIS OF STERIOD COMPOUNDS AND SUBSTANCES RELATED TO THEM

XXXII. STEREOCHEMISTRY OF THE HYDROGENATION AND REDUCTION OF 6, 9-DIMETHYL-1-KETO-$\Delta^{4\,(10),5}$ - HEXAHYDRONAPHTHALENE

I. N. Nazarov, S. N. Ananchenko and I. V. Torgov

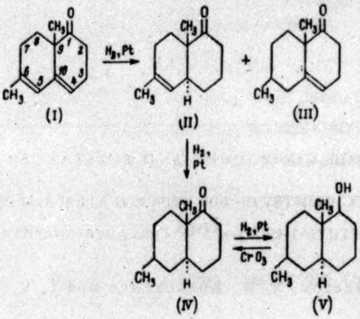
In a previous communication [1] we described a new reaction for the intramolecular condensation of cyclic 1,3-diketones with an allyl side chain. In part, we obtained in this manner 6,9-dimethyl-1-keto-$\Delta^{4\,(10),\,5}$-hexahydronaphthalene (I), starting from methyldihydroresorcinol and γ, γ-dimethylallyl bromide:



(I)

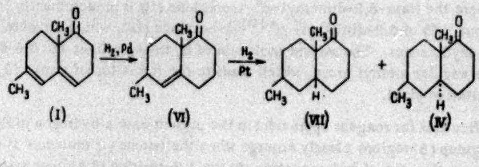
It seemed of interest to study the spatial direction of the hydrogenation and reduction of 6,9-dimethyl-1-keto- $\Delta^{4\,(10),\,5}$-hexahydronaphthalene (I), which shows significance for the stereochemistry of cyclic compounds and the synthesis of steroids with a definite spatial configuration. It was revealed that the addition of the first molecule of hydrogen to ketone (I), in the presence of a platinum catalyst and in either alcohol or glacial acetic acid solution, proceeds mainly at the 4, 10 double bond on the side opposite to the angular methyl group, and here the trans-6,9-dimethyl-Δ^{5}-1-octalone (II) is predominantly formed, together with a small amount (about 5%) of 6,9-dimethyl- $\Delta^{4\,(10)}$-1-octalone (III), which we were able to separate through the 2,4-dinitrophenylhydrazones. The second molecule of hydrogen adds at the 5,6-double bond, also on the side opposite the angular methyl group, which leads to the formation of trans- 6β, 9-dimethyl-1-decalone (IV) in almost quantitative yield.

The steric difficulties for reagent approach (in the present case a hydrogen molecule) from the side of the angular methyl group (β-region) clearly emerge when the ketone (I) molecule is examined on a Stuart model; consequently, in the case of hydrogenation (in the 1,2-position of a diene system) the trans-ketone (II) should be formed. Further hydrogenation of ketone (II), as again follows from the model, should also proceed selectively due to the presence of steric hindrance in the β-region and should lead predominantly to ketone (IV). When 6,9-dimethyl-1-keto- $\Delta^{4,5}$-hexahydronaphthalene (I) is subjected to exhaustive hydrogenation in the presence of a platinum catalyst 3 molecules of hydrogen are absorbed and the crystalline trans- 6β,9-dimethyl-1β-decalol (V) is formed, the oxidation of which with chromic mixture gives the above-mentioned trans-6β, 9-dimethyl-1-decalone (IV):

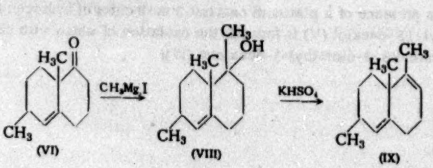


The exhaustive hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) to trans-6β,9-dimethyl-1-decalol (V) proceeds most easily with a platinum catalyst in the presence of hydrochloric acid, which accelerates reduction of the carbonyl group. When ketone (I) is hydrogenated with platinum catalyst in the absence of hydrochloric acid (in either alcohol or acetic acid solution) only the first 2 molecules of hydrogen show rapid addition to the ethylene bonds, while the third molecule, going for reduction of the the carbonyl group, adds at a rate that is several times slower.

The addition of the first molecule of hydrogen to ketone (I) in the presence of palladium catalyst in alcohol solution occurs at the 1,4-position of the diene system with the formation of 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI), after which the hydrogenation slows up sharply. Further hydrogenation of the 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) with a platinum catalyst is no longer characterized by spatial selectivity, and here a mixture of equal amounts of the cis- and trans- 6β,9-dimethyl-1-decalones (VII) and (IV) is formed, separated through the 2,4-dinitrophenylhydrazones:



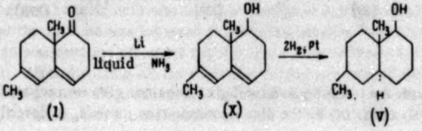
The reaction of methylmagnesium iodide with 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) gives 1,6β,9-trimethyl-$\Delta^{5(10)}$-1-octalol (VIII) in high yield, the dehydration of which with potassium bisulfate gives 1,6β,9-trimethyl-$\Delta^{1,5(10)}$-hexahydronaphthalene (IX):



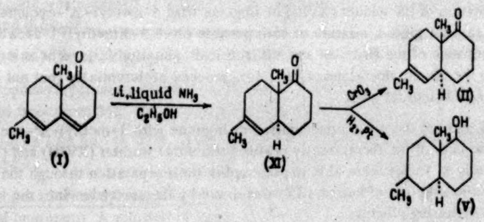
In the ozonolysis products of the latter we failed to find even traces of either acetic or malonic acid, which together with the hydrogenation of the 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) to the cis- and trans-6β,9-dimethyldecalones (VII) and (IV), shows that the double bond in 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) is found at the 5,10-position, and not the 4,10.

The hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) in the presence of a nickel catalyst, in contrast to platinum and palladium, fails to show a selective character. After adding two molecules of hydrogen (the hydrogenation is very slow) we were able to isolate the crystalline trans-6β,9-dimethyl-1-decalol (V) in about 20% yield. Here the main portion of the substance remained as a liquid mixture, which was not investigated further.

Only the carbonyl group is involved when ketone (I) is reduced with lithium in liquid ammonia and 6,9-dimethyl-$\Delta^{4(10),5}$-1-hexalol (X) is formed in 70% yield, the hydrogenation of which with platinum catalyst gave the above-described trans-6β,9-dimethyl-1-decalol (V):



If the reduction of ketone (I) with lithium in liquid ammonia is run in the presence of alcohol, then here not only the carbonyl group is involved, but also the double bond in the 4,10-position. As a result the trans-6,9-dimethyl-Δ^5-1-octalol (XI) is formed in 52% yield, the oxidation of which with chromic anhydride gave the trans-6,9-dimethyl-Δ^5-1-octalone (II), while when hydrogenated with platinum catalyst the above described trans-6β,9-dimethyl-1β-decalol (V) is formed:

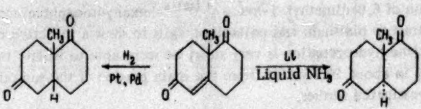


All of the specimens of the trans-6β,9-dimethyl-1-decalol (V) described in this paper give the same 3,5-dinitrobenzoate with m. p. 128-129°, and when oxidized with chromic anhydride are transformed into the same trans-6β,9-dimethyl-1-decalone (IV), giving a 2,4-dinitrophenylhydrazone with m. p. 212°.

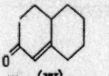
As a result, the very interesting fact was established that the catalytic hydrogenation (especially with platinum), and also the reduction with lithium in liquid ammonia, of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) and its corresponding alcohol (X), proceed with spatial selectivity, and here only the derivatives of trans-decalin are formed with a definite (β) orientation of the methyl group at C_6 and of the hydroxyl at C_1.

In contrast to Compounds (I) and (X) with a heteroannular 1,4-diene system, the catalytic hydrogenation of 9-methyl-1,6-diketo-Δ^5-octalin (XII) leads to the formation of only the cis-9-methyl-1,6-diketodecalin (XIII), while the trans-isomer (XIV) is formed only when the diketooctalin (XII) is reduced with lithium in liquid ammonia [2].

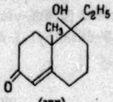
For comparison it should be mentioned that the catalytic hydrogenation of the Δ^5-6-octalones (XV) and (XVI) leads to the formation of a mixture of the corresponding cis- and trans-decalin derivatives with the cis-decalin compounds predominating [2,3], whereas the hydrogenation of the enol ether of the Δ^5-6-oxtalone (XVII) leads to the predominant formation of the trans-decalin derivative [4]:



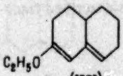
(XIII) (XII) (XIV)



(XV)

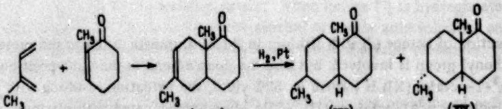


(XVI)



(XVII)

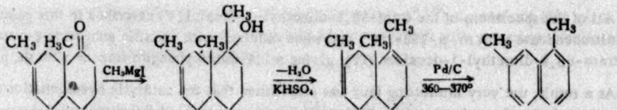
For comparison with the trans-6β,9-dimethyl-1-decalone (IV) we prepared both of the cis-6,9-dimethyl-1-decalone epimers (VII) and (XIX) by the diene condensation method, as described earlier [5]:



(XVIII) (VII) (XIX)

The hydrogenation of the adduct (XVIII) of isoprene with 1-methyl-Δ^1-cyclohexen-6-one in the presence of platinum catalyst gives a mixture of both possible cis-6,9-dimethyl-1-decalone isomers (VII) and (XIX), with predominance of the first. As a result, this hydrogenation fails to be selective, although the addition of hydrogen to the dimethyloctalone (XVIII) does proceed preferentially (but not exclusively) from the side opposite the angular methyl group.,

In a detailed study of the diene condensation of isoprene with 1-methyl-Δ^1-cyclohexen-6-one it was established that here both of the theoretically possible structural isomers (XVIII) and (XX) are formed in the ratio of approximately 6 : 1. We were able to accomplish their separation through the 2,4-dinitrophenylhydrazones,, while the structure of ketone (XX) was shown by its conversion into the known 1,7-dimethylnaphthalene by the following scheme:



(XX) (XXI) (XXII)

As a result, the structural direction of the diene condensation of isoprene with 1-methyl-Δ^1-cyclohexen-6-one obeys the usual rules established for 2-substituted dienes with unsymmetrical dienophils [6].

EXPERIMENTAL

Hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with Pt catalyst (3 moles of hydrogen): a solution of 0.3 g of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with m. p. 49-50° in 8 ml of ethyl alcohol was hydrogenated in the presence of platinum oxide. After 3 hours the hydrogen absorbed was 120 ml against a theory of 114 ml (based on 3 moles).

The residue crystallized after distilling off the solvent. Its recrystallization from petroleum ether gave 0.24 g of trans-6β,9-dimethyl-1-decalol (V) with m. p. 94°.

Found %: C 79.03, 79.08; H 12.06, 11.98. $C_{12}H_{22}O$. Calculated %: C 79.05; H 12.16.

The 3,5-dinitrobenzoate melts at 128-129° (from petroleum ether).

Found %: C 60.68; H 6.69. $C_{19}H_{24}O_6N_2$. Calculated %: 60.62; H 6.43.

Oxidation of trans-6β,9-dimethyl-1-decalol (V). To a solution of 88 mg of the trans-6β,9-dimethyl-1-decalol (V) in 3 ml of glacial acetic acid was added a solution of 0.1 g of chromic anhydride in 5 ml of glacial acetic acid and the mixture was let stand at room temperature for 48 hours. Then 2 ml of alcohol was added, the acetic acid was distilled off under slight vacuum, the residue was treated with water, and then extracted with ether. After distilling off the ether the residue was treated with 2,4-dinitrophenylhydrazine solution and gave the 2,4-dinitrophenylhydrazone of trans-6β,9-dimethyl-1-decalone (IV) with m. p. 212-213° (from a 1:1 mixture of alcohol and benzene).

Selective hydrogenation of 6, 9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with Pt catalyst in alcohol (2 moles of hydrogen). A solution of 0.5 g of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene in 10 ml of alcohol was hydrogenated in the presence of platinum oxide. The amount of hydrogen absorbed after 45 minutes was 130 ml against a theoretical of 127 ml (based on 2 moles of hydrogen). After distilling off the solvent the residue was distilled and gave 0.4 g of the trans-6β,9-dimethyl-1-decalone (IV).

B. p. 92-93° (1 mm), n_D^{18} 1.4854, $\lambda_{max.}$ (in isooctane) 296, 304 mμ.

Found %: C 79.90, 79.90; H 11.24, 11.11. $C_{12}H_{20}O$. Calculated %: C 79.94; H 11.18.

The semicarbazone was obtained as white crystals, melting with decomposition at 215-216° (from a mixture of alcohol and dioxane).

Found %: N 17.80, 18.10. $C_{13}H_{23}ON_3$. Calculated %: N 17.86.

The 2,4-dinitrophenylhydrazone of ketone (IV) melts at 212° (from a 1:1 mixture of alcohol and benzene), $\lambda_{max.}$ (in isooctane) 345, 426 mμ (ε $1.99 \cdot 10^4$, $0.532 \cdot 10^4$).

Found %: C 59.83, 59.89; H 6.70, 6.83; N 15.64, 15.55. $C_{18}H_{24}O_4N_4$. Calculated %: C 59.98; H 6.71; N 15.54.

Selective hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with Pt catalyst in alcohol (1 mole of hydrogen). A solution of 1.5 g of ketone (I) in 15 ml of alcohol was hydrogenated. The amount of hydrogen absorbed in 30 minutes was 190 ml (1 mole), and the hydrogenation was stopped. The catalyst was filtered and after distilling off the solvent we obtained 1.4 g of mixed trans-6,9-dimethyl-Δ^5-1-octalone (II) and 6,9-dimethyl-$\Delta^{4(10)}$-1-octalone (III). From this mixture of ketones we prepared the 2,4-dinitrophenylhydrazones. Using the method of fractional crystallization from a mixture of alcohol and ethyl acetate (1:1) we isolated 2 g of the 2,4-dinitrophenylhydrazone of trans-6,9-dimethyl-Δ^5-1-octalone (II) with m. p. 207-208.5°.

Found %: C 60.55, 60.66; H 6.21, 6.15; N 16.00, 15.89. $C_{18}H_{22}O_4N_4$. Calculated %: C 60.67; H 6.19; N 15.63.

In addition, we obtained 0.1 g of the 2,4-dinitrophenylhydrazone of 6,9-dimethyl-$\Delta^{4(10)}$-1-octalone (III) with m. p. 189-190°.

Found %: N 15.46, 15.68. $C_{18}H_{22}O_4N_4$. Calculated %: N 15.63.

Hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with Pt catalyst in glacial acetic acid. A solution of 1.25 g of ketone (I) in 15 ml of glacial acetic acid was hydrogenated in the presence of platinum oxide. The amount of hydrogen absorbed in 75 minutes was 325 ml against the 320 ml required by theory (based on 2 moles of hydrogen), after which the hydrogenation was stopped. After distilling off the solvent the residue was distilled and gave 0.9 g of trans-6β,9-dimethyl-1-decalone (IV) with b. p. 91-93° (1 mm), n_D^{20} 1.4860. Its 2,4-dinitrophenylhydrazone melted at 210-212° and failed to give a depression when mixed with the specimen obtained in a previous experiment.

Hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with Pt catalyst in alcohol in the presence of hydrochloric acid. A solution of 0.22 g of ketone (I) in 10 ml of alcohol and 3 ml of concentrated hydrochloric acid was hydrogenated in the presence of platinum oxide. The amount of hydrogen absorbed in 40 minutes was 88 ml against the 77 ml required by theory (based on 3 moles). The solvent was distilled under slight vacuum, and the residue was extracted with ether, the ether extract washed with water, and dried over magnesium sulfate. The residue crystallized after distilling off the ether. It was recrystallized from petroleum ether and here we obtained 0.17 g of trans-6β,9-dimethyl-1-decalol (V) with m. p. 96-98°, failing to give a depression with the specimen from a previous experiment. The 3,5-dinitrobenzoate melted at 128-129° (from petroleum ether) and also failed to give a depression with the specimen from a previous experiment.

6,9-Dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronapthalene (I) fails to hydrogenate in the presence of platinum oxide when dissolved in pyridine, in alcoholic potassium hydroxide solution, and also in alcohol in the presence of sodium hydroxide traces.

Hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) in the presence of nickel catalyst. A solution of 1 g of ketone (I) in 10 ml of alcohol was hydrogenated in the presence of Raney nickel. The amount of hydrogen absorbed in 28 hours was 260 ml against the 254 ml required by theory (based on 2 moles). The hydrogenation was stopped, and after distilling off the solvent the residue partially crystallized. We obtained 0.19 g of the trans-6β,9-dimethyl-1-decalol (V) with m.p. 92-94°. The mother liquor (n_D^{20} 1.5020) was not investigated.

Hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) in the presence of Pd catalyst. A solution of 1.8 g of ketone (I) in 15 ml of alcohol was hydrogenated in the presence of palladium on calcium carbonate (10% Pd). The amount of hydrogen absorbed in 25 minutes was 255 ml against the 230 ml required by theory (based on 1 mole), after which the hydrogenation rate showed sharp reduction, and the catalyst was removed. After removing the solvent by distillation the residue was vacuum distilled and gave 1.5 g of the 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI).

B. p. 85-87° (1.5 mm), n_D^{20} 1.5000, $\lambda_{max.}$ (in isooctane) 298, 307, 318 mμ.

Found %: C 80.52, 80.50; H 10.26, 10.30. $C_{12}H_{18}O$. Calculated %: C 80.80; H 10.11.

The 2,4-dinitrophenylhydrazone of ketone (VI) melts with decomposition at 200-201° (from a 1:1 mixture of ethyl alcohol and ethyl acetate), $\lambda_{max.}$ (in isooctane) 350, 428 mμ.

Found %: N 15.50, 15.58. $C_{18}H_{22}O_4N_4$. Calculated %: N 15.63.

Its mixture with the 2,4-dinitrophenylhydrazone of 6,9-dimethyl-$\Delta^{4(10)}$-1-octalone (III) melted at 183°.

Reaction of 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) with methylmagnesium iodide. Proceeding from 0.8 g of magnesium, 5 g of methyl iodide and 40 ml of absolute ether a solution of methylmagnesium iodide was prepared in a three-necked flask, fitted with stirrer, dropping funnel and reflux condenser. To the cooled Grignard reagent solution was added 2 g of 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) in 15 ml of absolute ether. The reaction mixture was heated for 4 hours at 35-40° and then treated with dilute (1:1) hydrochloric acid. The ether layer was separated, dried over magnesium sulfate, the ether removed by distillation, and the residue vacuum distilled. We obtained 1.8 g of 1,6β,9-trimethyl-$\Delta^{5(10)}$-1-octalol (VIII) with b. p. 97-100° (2 mm), n_D^{20} 1.5070.

Found %: C 80.45, 80.34; H 11.51, 11.50. $C_{13}H_{22}O$. Calculated %: C 80.41; H 11.30.

Dehydration of 1, 6β,9-Trimethyl-$\Delta^{5(10)}$-1-octalol (VIII). A mixture of 1.8 g of (VIII) and 0.6 g of potassium bisulfate was heated at 150-160° for 40 minutes. The product was treated with water, extracted with ether, dried over sodium sulfate, and vacuum distilled. We obtained 1 g of 1,6β,9-trimethyl-$\Delta^{1(2);5(10)}$-hexahydronaphthalene (IX) with b. p. 63-65° (2 mm), n_D^{20} 1.5010.

The obtained hydrocarbon was ozonized in chloroform solution at 0° for 3 hours. The ozonide was decomposed in the presence of hydrogen peroxide under heating for 8 hours. From the neutral products after extraction with ether (after neutralization with soda) was isolated 0.1 g of viscous oil failing to crystallize. The aqueous solution was acidified with concentrated hydrochloric acid (until acid to Congo) and then extracted with ether. A thick oil remained after distilling off the ether, which gave a negative test for malonic acid (heating with acetic anhydride) and acetic acid (cacodyl test).

Hydrogenation of 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI). A solution of 1 g of ketone (VI) in 15 ml of alcohol was hydrogenated in the presence of platinum oxide. The amount of hydrogen absorbed in 4 hours was 125 ml against the 125 ml required by theory (based on 1 mole). The hydrogenation was stopped, the alcohol was distilled off, the residue was vacuum distilled, and we obtained 0.9 g of mixed cis- and trans-6β,9-dimethyl-1-decalones (VII) and (IV) with b. p. 90-92° (1 mm), n_D^{20} 1.4865. From 0.9 g of this ketone mixture we prepared the 2,4-dinitrophenylhydrazones. Using the method of successive fractional crystallization from a mixture of alcohol and ethyl acetate (1: 1) we isolated the 2,4-dinitrophenylhydrazone of trans-6β,9-dimethyl-1-decalone (IV) with m. p. 210-212° (fails to give a melting point depression with the specimen described above) and the 2,4-dinitrophenylhydrazone of cis-6β,9-dimethyl-1-decalone (VII) with m. p. 182-183°, which also failed to show a depression with the authentic specimen (see below). Practically equal amounts of the two 2,4-dinitrophenylhydrazones were obtained.

Reduction of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with lithium in liquid ammonia. Into a three-necked flask, fitted with mechanical stirrer, dropping funnel and thermometer, and cooled to −70°, was distilled 100-120 ml of ammonia, after which 0.2 g of lithium was added and the mixture stirred at −70° for 20 minutes; then 1 g of ketone (I) in 15 ml of absolute ether was added and the stirring continued for another 2 hours. Here the reaction mass failed to decolorize. Five grams of ammonium chloride was added and the mixture stirred, gradually raising the temperature from −70° to room temperature. The product was treated with water, extracted with ether, and dried over magnesium sulfate. After distilling off the ether the residue was vacuum distilled and gave 0.7 g of 6,9-dimethyl-$\Delta^{4(10),5}$-hexahydronaphthalene-1-ol (X) as a viscous yellow liquid with b. p. 105-106° (3 mm), n_D^{20} 1.5410, yield 70%.

Found %: C 81.18, 80.94; H 9.75, 9.78. $C_{12}H_{18}O$. Calculated %: C 80.80; H 10.11.

Hydrogenation of 6,9-dimethyl-$\Delta^{4(10),5}$-hexahydronaphthalene-1-ol (X). A solution of 0.6 g of carbinol (X) in 15 ml of alcohol was hydrogenated with platinum oxide. The amount of hydrogen absorbed in 30 minutes was 161 ml against the 150 ml required by theory (based on 2 moles). The residue crystallized after distilling off the solvent. Recrystallization from petroleum ether gave 0.25 g of trans-6β,9-dimethyl-1-decalol (V) with m. p. 100°, which failed to show a depression with the specimen described above, melting at 93-94°. The 3,5-dinitrobenzoate melted at 128-129° and also failed to show a depression with the 3,5-dinitrobenzoate, obtained from the specimen with m. p. 93-94°. Oxidation of the obtained trans-6β,9-dimethyl-1-decalol (V) with chromic anhydride in glacial acetic acid (under the conditions described above) gave a product that yielded only one 2,4-dinitrophenylhydrazone when reacted with 2,4-dinitrophenylhydrazine, corresponding to that of trans-6β,9-dimethyl-1-decalone (IV) with m. p. 212-213°.

Reduction of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) with lithium in liquid ammonia in the presence of alcohol. Into a three-necked flask, fitted with mechanical stirrer, dropping funnel and thermometer, and cooled to −70°, was distilled 140-150 ml of ammonia. Then 0.6 g of lithium was added and the mixture stirred for 20 minutes at −70°, after which 2.1 g of ketone (I) in 40 ml of absolute ether was added and stirring continued for another 35 minutes. Then 15 ml of absolute alcohol was added (the solution became colorless when 11 ml of alcohol was added), the mixture stirred for 2 hours at −70°, and then 10 g of ammonium chloride was added. The ammonia was evaporated, and the residue was treated with water, extracted with ether, and the extract dried over sodium sulfate. After distilling off the ether the residue crystallized completely. We obtained 1.1 g of crystals with m. p. 85-87°. Recrystallization from petroleum ether gave 0.9 g of 6,9-dimethyl-$\Delta^{5(6)}$-1-octalol (XI) with m. p. 87-89°. Yield 52%.

Found %: C 79.93, 80.08; H 11.24, 11.35. $C_{12}H_{20}O$. Calculated %: C 79.94; H 11.18.

Oxidation of 6,9-dimethyl-$\Delta^{5(6)}$-1-octalol (XI). A mixture of 0.3 g of carbinol (XI) in 5 ml of glacial acetic acid and 0.6 g of chromic anhydride in 40 ml of glacial acetic acid was let stand at room temperature for 48 hours. After the usual treatment we obtained 0.1 g of 6,9-dimethyl-Δ^{5}-1-octalone (II) with b. p. 79-82° (2 mm), n_D^{20} 1.5010. Its 2,4-dinitrophenylhydrazone melted with decomposition at 206-208° (from a 1:1 mixture of alcohol and ethyl acetate) and failed to show a depression with the specimen described above. Its mixture with the 2,4-dinitrophenylhydrazone of 6β,9-dimethyl-$\Delta^{5(10)}$-1-octalone (VI) melted at 198-202° with decomposition.

Hydrogenation of 6,9-dimethyl-$\Delta^{5(6)}$-1-octalol (XI). A solution of 0.33 g of carbinol (XI) in 20 ml of alcohol was hydrogenated in the presence of PtO_2. The amount of hydrogen absorbed in 1 hour was 60 ml against the 50 ml required by theory (based on 1 mole). After distilling off the solvent the residue crystallized. Weight 0.27 g, m. p. 87-90°. Recrystallization from petroleum ether gave 0.203 g of the trans-6β,9-dimethyl-1-decalol (V) with m. p. 94°. Its 3,5-dinitrobenzoate melted at 128-129°. Oxidation of the obtained alcohol (V) with chromic anhydride in glacial acetic acid, followed by treatment of the resulting trans-6β,9-dimethyl-1-decalone (IV) with 2,4-dinitrophenylhydrazine solution, gave the 2,4-dinitrophenylhydrazone of (IV) with m. p. 211-212°.

The condensation of isoprene with 1-methyl-Δ^{1}-cyclohexen-6-one was run by our earlier developed method [5]. A mixture of 30 g of isoprene and 135 g of 1-methyl-Δ^{1}-cyclohexen-6-one was heated in a metal ampul for 50 minutes at a bath temperature of 280-285°. The unreacted 1-methyl-Δ^{1}-cyclohexen-6-one was vacuum distilled (123 g, b. p. 55-60° (10 mm), n_D^{20} 1.4835). From three similar experiments we obtained 20 g of condensation products (XVIII) and (XX) with b. p. 80-85° (2 mm), n_D^{20} 1.5030.

From 10 g of condensation products we obtained 13 g of mixed (XVIII) and (XX) 2,4-dinitrophenylhydrazones, proceeding from 10.4 g of 2,4-dinitrophenylhydrazine, 500 ml of alcohol, 50 ml of dioxane and 12 ml of hydrochloric acid. Using the method of successive fractional crystallization from a mixture of ethyl acetate and alcohol we isolated from this mixture 6 g of the 2,4-dinitrophenylhydrazone of cis-6,9-dimethyl-Δ^{6}-1-octalone (XVIII).

M. p. 181-182°, $\lambda_{max.}$ (in isooctane) 346, 428 mμ.

Found %: N 15.69, 15.67. $C_{18}H_{22}O_4N_4$. Calculated %: N 15.63.

We also isolated 1.02 g of the 2,4-dinitrophenylhydrazone of cis-7,9-dimethyl-Δ^{6}-1-octalone (XX) with m. p. 162.5-163°.

Found %: C 60.56, 60.54; H 6.20, 6.05; N 15.84, 15.71. $C_{18}H_{22}O_4N_4$. Calculated %: C 60.67; H 6.19; N 15.63.

The mixture of the two hydrazones shows a sharp depression of the melting point (m. p. 130-140°).

Hydrolysis of the 2,4-dinitrophenylhydrazone of cis-6,9-dimethyl-Δ^{6}-1-octalone (XVIII). A mixture of 4 g of hydrazone (XVIII) (m. p. 182-183°), 8 ml of pyrotartaric acid (10-fold excess), 9.6 g of sodium acetate, 100 ml of water and 260 ml of acetic acid was heated for 2 hours at 110-120° (the hydrazone dissolved completely after 1 hour). The acetic acid was vacuum distilled to incipient crystallization of the 2,4-dinitrophenylhydrazone of pyrotartaric acid. The residue was treated with saturated soda solution (to weak alkaline reaction), the 2,4-dinitrophenylhydrazone of pyrotartaric acid removed by filtration, and the precipitate thoroughly washed with ether. The filtrate was also extracted with ether. The ether was distilled off, and the residue was vacuum distilled to give 1.6 g of the cis-6,9-dimethyl-Δ^{6}-1-octalone (XVIII) with b. p. 82-83° (2 mm), $n_D^{20.5}$ 1.5005, yield 80%. The semicarbazone melts at 218-220° (with decomp.) and fails to show a melting point depression with the semicarbazone obtained earlier [5].

Hydrogenation of cis-6,9-dimethyl-Δ^{6}-1-octalone (XVIII). A solution of 1.6 g of the above-obtained cis-6,9-dimethyl-Δ^{6}-1-octalone in 25 ml of alcohol was hydrogenated in the presence of platinum oxide. The amount of hydrogen absorbed in 23 hours was 312 ml against the 290 ml required by theory (based on 3 moles). The solvent was distilled off, and the residue was vacuum distilled to give 1.2 g of the cis-6,9-dimethyl-1-decalol with b. p. 94-96° (1 mm), n_D^{20} 1.4960.

Found %: C 79.40, 79.23; H 11.56, 11.60. $C_{12}H_{22}O$. Calculated %: C 79.05; H 12.01.

The obtained alcohol was oxidized with chromic anhydride in acetic acid and gave 0.8 g of mixed cis-6,9-dimethyl-1-decalone (VII) and (XIX) with b. p. 90-93° (1 mm), n_D^{20} 1.4870. From this mixture of ketones we obtained 1.2 g of 2,4-dinitrophenylhydrazones. Successive fractional crystallization from alcohol and ethyl acetate gave 0.3 g of the 2,4-dinitrophenylhydrazone of cis-6β,9-dimethyl-1-decalone (VII).

B. p. 181-182°, $\lambda_{max.}$ (in isooctane) 348, 424 mμ (ϵ $1.85 \cdot 10^4$, $0.392 \cdot 10^4$).

Found %: C 60.06, 69.18; H 7.04, 6.99; N 15.47, 15.57. $C_{18}H_{24}O_4N_4$. Calculated %: C 59.98; H 6.71; N 15.54.

This hydrazone gives a sharp melting point depression with the 2,4-dinitrophenylhydrazone of cis-6,9-dimethyl-Δ^6-1-octalone (XVIII) (to 140-145°) and fails to show a melting point depression with Specimen (VII), described above. We also isolated 0.1 g of 2,4-dinitrophenylhydrazone of the cis-6α,9-dimethyl-1-decalone (XIX).

B. p. 152-153.5°, $\lambda_{max.}$ (in isooctane) 347, 424 mμ (ϵ $1.77 \cdot 10^4$, $0.392 \cdot 10^4$).

Found %: C 59.82, 59.72; H 6.76, 6.56; N 15.59, 15.40. $C_{18}H_{24}O_4N_4$. Calculated %: C 59.98; H 6.71; N 15.54.

Hydrolysis of the 2,4-dinitrophenylhydrazone of cis-7,9-dimethyl-Δ^6-1-octalone (XX). A mixture of 2.1 g of the 2,4-dinitrophenylhydrazone of cis-7,9-dimethyl-Δ^6-1-octalone (XX) (m. p. 162-163°), 4 ml of pyrotartaric acid (9-fold excess), 4.6 g of sodium acetate, 130 ml of acetic acid and 100 ml of water was heated for 3 hours at 110-115°. After treatment, similar to the above, we obtained 0.8 g of cis-7,9-dimethyl-Δ^6-1-octalone (XX) with b. p. 83-84° (2 mm), n_D^{20} 1.5008, yield 75%.

Reaction of cis-7,9-dimethyl-Δ^6-1-octalone (XX) with methylmagnesium iodide. Proceeding from 0.3 g of magnesium, 2 g of methyl iodide and 20 ml of absolute ether, a solution of methylmagnesium iodide (a 3-fold excess of the reagent) was prepared in a three-necked flask, fitted with mechanical stirrer, dropping funnel and reflux condenser. To the Grignard reagent was added 0.8 g of cis-7,9-dimethyl-Δ^6-1-octalone (XX) in 10 ml of absolute ether and the mixture heated for 1 hour at 35-40°. The product was treated with 5 ml of dilute (1:1) hydrochloric acid, extracted with ether, and vacuum distilled. We obtained 0.6 g of cis-1,7,9-trimethyl-Δ^6-1-octalol (XXI) with b. p. 96-100° (2 mm), n_D^{20} 1.5110.

Dehydration of 1,7,9-trimethyl-Δ^6-1-octalol (XXI). A mixture of 0.6 g of 1,7,9-trimethyl-Δ^6-1-octalol (XXI) and 0.2 g of freshly ignited potassium bisulfate was heated for 1 hour at 150-160°. The product was treated with water, extracted with ether, and vacuum distilled. We obtained 0.35 g of 1,7,9-trimethyl-$\Delta^{1,6}$-hexahydronaphthalene (XXII) with b. p. 63-65° (1 mm), n_D^{20} 1.5030.

Dehydrogenation of 1,7,9-trimethyl-$\Delta^{1,6}$-hexahydronaphthalene (XXII). A solution of 0.35 g of 1,7,9-trimethyl-$\Delta^{1,6}$-hexahydronaphthalene (XXII) in 10 ml of dry benzene and 0.2 g of 10% palladium on charcoal was heated in a rotated autoclave in a nitrogen atmosphere for 21 hours at 360-370°. The catalyst was filtered, the solvent vacuum distilled, and the residue treated with 143 g of picric acid in 3 ml of alcohol. We obtained 112 mg of the picrate of 1,7-dimethylnaphthalene with m. p. 115.5-117°. After recrystallization from alcohol the picrate melted at 119-120°. It shows a melting point depression with picric acid (m. p. 100-105°) and with the picrate of 1,6-dimethylnaphthalene (m. p. 96-99°). From the literature the picrate of 1,7-dimethylnaphthalene melts at 121° [7].

SUMMARY

The catalytic hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) in the presence of a platinum catalyst, and also its reduction with lithium in liquid ammonia, are strictly selective, and lead to the formation of only trans-6β,9-dimethyldecalin derivatives. The first molecule of hydrogen adds to the 4,10 double bond on the side opposite the angular methyl group, while the second molecule of hydrogen adds to the 5,6 double bond, also on the side opposite the angular methyl group (leading to the formation of trans-6β,9-dimethyldecalin derivatives).

The hydrogenation of 6,9-dimethyl-1-keto-$\Delta^{4(10),5}$-hexahydronaphthalene (I) in the presence of Pd catalyst proceeds by the mechanism of 1,4-addition, while in the presence of a Ni catalyst this hydrogenation fails to show a selective character in the sequence of reactions, but also leads only to the trans-decalin derivative.

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* T. p. = C. B. Translation pagination.

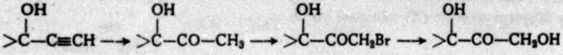
SYNTHESIS OF STEROID COMPOUNDS AND SUBSTANCES RELATED TO THEM

XXXIII. THE SIMPLER ANALOGS OF CORTICOSTEROIDS.

1. METHODS OF INTRODUCING THE DIHYDROXYACETONE, GLYCEROL AND DIHYDROXYPROPANECARBOXYLIC SIDE CHAINS IN CYCLIC COMPOUNDS

I. N. Nazarov and A. A. Akhrem

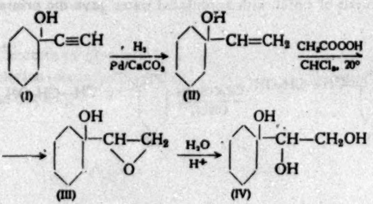
In recent times the complete synthesis of cortisone and its simpler analogs has attracted the attention of many synthetic organic chemists [1]. An important step of this synthesis is the construction of the dihydroxyacetone and glycerol side chains, characteristic for most hormones of the adrenal cortex. At the present time the cyanohydrin method of introducing a dihydroxyacetone side chain has been studied most completely, and also the method based on the hydration of acetylene alcohols to the corresponding α-ketols, with subsequent bromination and saponification of the α-bromoketols to the dihydroxyacetone derivatives:



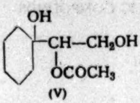
$$>\overset{OH}{\underset{|}{C}}-C{\equiv}CH \longrightarrow >\overset{OH}{\underset{|}{C}}-CO-CH_3 \longrightarrow >\overset{OH}{\underset{|}{C}}-COCH_2Br \longrightarrow >\overset{OH}{\underset{|}{C}}-CO-CH_2OH$$

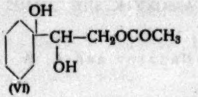
As is known [2], this method leads to obtaining steroid compounds with α-orientation of the side chain at C_{17}, whereas in natural-occurring compounds the dihydroxyacetone side chain (and in general all side chains at C_{17}) shows β-configuration. In addition, cases are known where isomerization is observed during hydration of acetylene alcohols, leading to expansion of the five-membered cycle to a six-membered, with formation of the so-called D-homosteroids and their analogs [3].

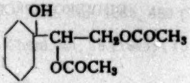
Having undertaken the task of systematically studying the synthesis of steroids and substances related to them, we set out several years ago to find new methods for building a dihydroxyacetone side chain, excluding the acetylene alcohol hydration step. We began our studies with the simpler cyclic ketones and as a model we used at first the readily available 1-ethynyl-1-cyclohexanol (I), obtained from cyclohexanone by the well-known Favorsky reaction:

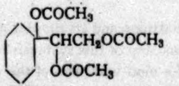


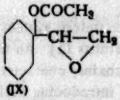
The catalytic hydrogenation of acetylene alcohol (I) with Pd-catalyst gave 1-vinyl-1-cyclohexanol (II) in high yield, the oxidation of which with peracetic acid in chloroform gave the corresponding glycidol (III) in about 80% yield. The treatment of the latter with dilute hydrochloric acid gave the crystalline triol (IV) in quantitative yield. Acidolysis of glycidol (III) with glacial acetic acid led to obtaining either monoacetate (V) or (VI) in good yield. Oxidation of the latter with chromic anhydride in either acetic acid or pyridine gave only water-soluble products, not extractable with ether, and here we were unable to isolate the ether-soluble, dihydroxyacetone derivative (XXIII) or its acetate. This oxidation result suggests that the monoacetate obtained in the acetolysis of glycidol (III) should have the structure of (V) with a primary hydroxyl group. Acetylation of the glycerol derivative (IV) with acetic anhydride in pyridine at 20° gave diacetate (VII) in 80% yield. Heating of the glycerol derivative (IV) with excess acetic anhydride in the presence of pyridine at 100-105° gave the corresponding triacetate (VIII) in about 60% yield. The latter was also obtained by boiling the glycidol (III) with acetic anhydride, but here there was also simultaneous formation of a small amount of the acetate of glycidol (IX).


(V)

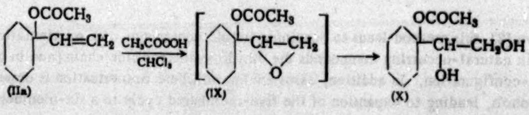

(VI)


(VII)


(VIII)

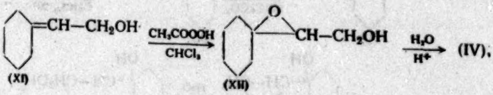

(IX)

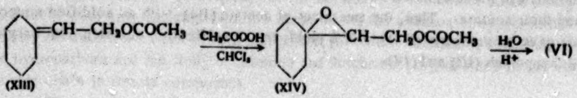
It is interesting to mention that the oxidation of the acetate of 1-vinyl-1-cyclohexanol (IIa) with peracetic acid in chloroform gave instead of the expected acetate of glycidol (IX) the product of its hydrolysis – the tertiary dihydroxyacetate (X) – in good yield:



The allyl isomerization of vinyl alcohol (II) with trichloroacetic acid [4] gave in 40-50% yield the corresponding primary alcohol – cyclohexylideneethanol (XI). Oxidation of the latter with peracetic acid gave the glycidol (XII) in 60% yield, the hydrolysis of which led to obtaining the above-described crystalline glycerol derivative (IV).

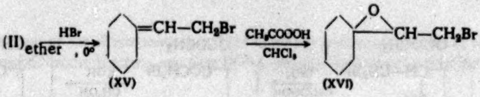
Oxidation of the acetate of the primary alcohol (XIII) under the same conditions gave the acetate of glycidol (XIV), the hydrolysis of which with acidulated water gave the primary dihydroxyacetate (VI):



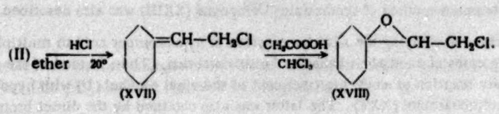

=CH—CH₂OCOCH₃
CH₃COOH
CHCl₃
O
CH—CH₂OCOCH₃
H₂O
H⁺
(VI)
(XIII)
(XIV)

A similar type of allyl isomerization of tertiary alcohols to primary alcohols, when an asymmetric carbon atom is present in the adjacent position and proceeding from compounds with an α-side chain, permits going, after oxidation and hydrolysis of the glycidol, to compounds with the necessary β-configuration for the side chain [5].

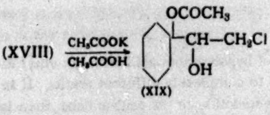
The allyl isomerization of vinyl alcohol (II) with hydrogen bromide in ether by the method developed in our laboratory [6] gave the primary allyl bromide (XV) in good yield, the oxidation of which with peracetic acid gave the bromohydrin of glycidol (XVI) in 80% yield:


(II)
HBr
ether, 0°
=CH—CH₂Br
CH₃COOOH
CHCl₃
O
CH—CH₂Br
(XV)
(XVI)

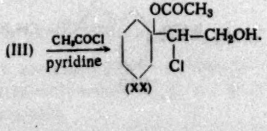
Under similar conditions the allyl chloride (XVII) gave the chlorohydrin of glycidol (XVIII) in 70% yield:


(II)
HCl
ether 20°
=CH—CH₂Cl
CH₃COOOH
CHCl₃
O
CH—CH₂Cl.
(XVII)
(XVIII)

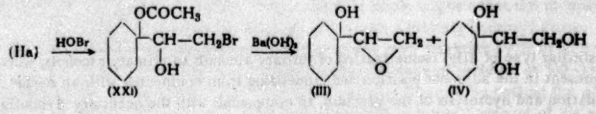
When an attempt was made to replace the chlorine atom in glycidol (XVIII) by the acetoxy group, using the method of heating it with potassium acetate in glacial acetic acid, there occurred opening of the glycidol oxide ring and the formation of a crystalline chlorine-containing product with m. p. 92-93°, to which we assign the structure of (XIX):


(XVIII)
CH₃COOK
CH₃COOH
OCOCH₃
CH—CH₂Cl
OH
(XIX)

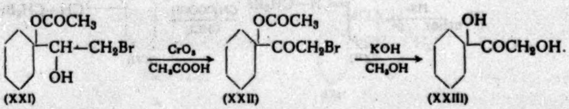
Instead of the expected acetate of glycidol (IX), the treatment of glycidol (III) with acetyl chloride in pyridine gave a crystalline chlorine-containing substance with m. p. 53-54°, isomeric with Compound (XIX), to which we assign the formula of (XX):


(III)
CH₃COCl
pyridine
OCOCH₃
CH—CH₂OH.
Cl
(XX)

The second method developed by us for introducing the dihydroxyacetone side chain in cyclic compounds is the bromohydrin method, based on the addition of the elements of hypobromous acid to cyclic vinyl compounds and their acetates. Thus, the treatment of acetate (IIa) with an acidified aqueous solution of bromoacetamide gave bromohydrin (XXI) in 95% yield, the saponification of which with baryta water gave the above described Compounds (III) and (IV):

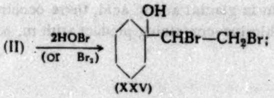


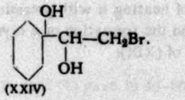
The oxidation of the bromohydrin (XXI) with chromic anhydride in acetic acid gave the bromoketol acetate (XXII) in good yield, also obtained by the bromination of the acetate of 1-acetyl-1-cyclohexanol. Saponification of the bromoketol (XXII) with alcoholic alkali gave the known 1-(ω-hydroxyacetyl)-1-cyclohexanol (XXIII) [7]:



When our work was concluded, there appeared a communication by the American investigators [8], in which the hypobromous method of synthesizing Compound (XXIII) was also described.

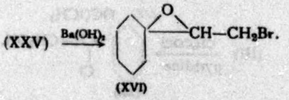
In the process of studying the addition reaction of hypobromous acid to multiple bonds we encountered some interesting cases of anomalous behavior for this reaction. Thus, instead of the expected bromohydrin (XXIV) as solitary reaction product, the treatment of the vinyl alcohol (II) with hypobromous acid also gave some of the dibromocarbinol (XXV). The latter was also obtained by the direct bromination of alcohol (II) with bromine in dry ether:





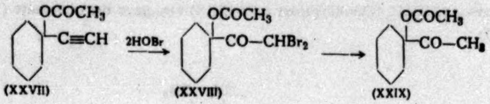
As a result, the reaction of hypobromous acid with the vinyl alcohol (II) and its acetate (IIa) proceeds by different mechanisms and leads to completely different results. If in the case of the vinyl alcohol acetate (IIa) the hypobromous acid adds smoothly to the double bond, then in the case of the vinyl alcohol itself (II), under the same conditions, there occurs only bromine addition to the double bond. As will be shown below, 1-ethynyl-1-cyclohexanol (I) and its acetate (XXVII) also show similar behavior toward hypobromous acid.

Saponification of the dibromocarbinol (XXV) with barious hydroxide gave the above described bromo oxide (XVI) in good yield.



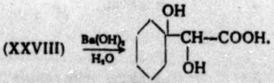
In 1952, when we approached the development of the bromohydrin method of constructing the dihydroxyacetone side chain, there were only two studies in the literature on the addition of hypobromous acid to a triple bond. This was, first, the known work of Favorsky and Vittorf [9] on the addition of hypobromous acid to substituted acetylene hydrocarbons and the study of Salomon and Reichstein [10], devoted to the building of the dihydroxyacetone side chain in steroid compounds.

The addition of two moles of hypobromous acid to the 1-ethynyl-1-cyclohexanol acetate (XXVII) gave us the dibromoketol acetate (XXVIII) in quantitative yield, the debromination of which with zinc dust in acetic acid gave the 1-acetyl-1-cyclohexanol acetate (XXIX), synthesized in our laboratory also by the hydration of acetate (XXVII):



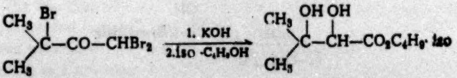
(XXVII) (XXVIII) (XXIX)

In the saponification of the dibromoketol acetate (XXVIII) with aqueous barium hydroxide solution there also proceeds simultaneous isomerization, and here the β-pentamethyleneglyceric acid (XXX) was obtained in 80% yield:



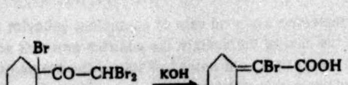
(XXX)

A similar isomerization on the example of the tribromo ketone (XXXI) under the influence of aqueous potassium hydroxide solution [11] was first observed by Favorsky in 1913:



(XXXI) (XXXII)

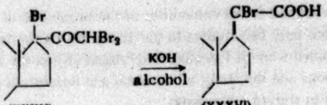
However, instead of the dihydroxy acid (XXX), the treatment of the cyclic tribromo ketone (XXXIII) with alcoholic potassium hydroxide [12] gave the corresponding acrylic acid derivative with bromine at the double bond (XXXIV).



(XXXIII) (XXXIV)

The treatment of (XXXIII) with aqueous KOH solution gave the dihydroxy acid (XXX) in 22% yield [12a].

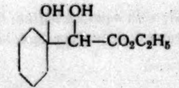
The unsaturated acid (XXXVI) with bromine at the double bond was also obtained in the case of the steroidal tribromo ketone (XXXV) [13], and consequently this method proved unsuitable for the introduction of glycerol side chains into cyclic compounds.



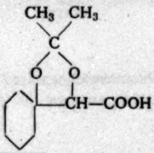
(XXXV) (XXXVI)

As a result, our described isomerization of the dibromo ketone acetate (XXVIII) into the β-pentamethyleneglyceric acid (XXX) opens a new way of obtaining substituted glyceric acids, which can show interest for the synthesis of corticoidal hormones and compounds related to them.

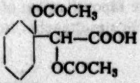
Treatment of the dihydroxy acid (XXX) with anhydrous ethanol in the presence of dry hydrogen chloride gave the ethyl ester (XXXVII). The dihydroxy acid (XXX) also gave the acetonate (XXXVIII) and the diacetate (XXXIX):



(XXXVII)



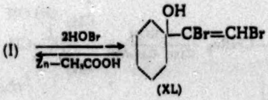
(XXXVIII)



(XXXIX)

The heating of the acid (XXX) above its melting point (above 118°) results in decomposition with the evolution of carbon dioxide and the formation of 1-cyclohexenylaldehyde [14].

Treatment of 1-ethynyl-1-cyclohexanol (I) with hypobromous acid gave, the same as in the case of the vinyl alcohol (II), the addition of two bromine atoms to the triple bond, and here the liquid unsaturated dibromide (XL) was obtained in high yield, in all probability having the trans-configuration:



(XL)

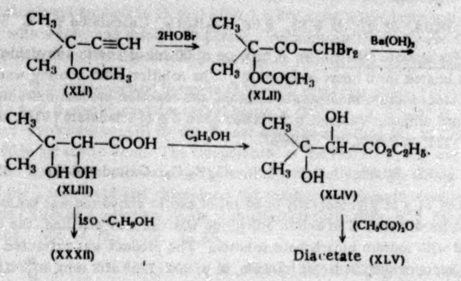
When heated with aqueous barium hydroxide solution the liquid trans-dibromide (XL) was completely transformed into the crystalline cis-isomer with m. p. 72-73°. The latter was also obtained by direct bromination of the acetylene alcohol (I) with bromine (1 mole) in dry carbon tetrachloride.

The above example represents a second case of anomalous behavior for the addition of hypobromous acid to multiple bonds. In the case of the acetate the addition proceeds normally, whereas the free hydroxyl group changes the reaction mechanism, and instead of adding the elements of hypobromous acid there occurs direct bromination of either the double or triple bond.

The debromination of the dibromide (XL) with zinc dust in glacial acetic acid gave the starting acetylenecarbinol (I). Here the debromination of the liquid isomer was accompanied by considerable heat effect, whereas the evolution of heat was not observed in the debromination of the crystalline isomer. The dehydration of the dibromide (XL) with potassium bisulfate gave a bromine-containing diene, which failed to show diene condensation with maleic anhydride.

The dimethylethynylcarbinol acetate (XLI) was transformed by the described reaction into the dibromoketol acetate (XLII). Treatment of the latter with barium hydroxide gave the β, β-dimethylglyceric acid

(XLIII), characterized as the ethyl ester (XLIV) and as the diacetate (XLV):



EXPERIMENTAL

The 1-ethynyl-1-cyclohexanol used in the experiments was obtained by the condensation of acetylene with cyclohexanone in the presence of powdered potassium hydroxide [15] and had the following constants: b. p. 77-78° at 15 mm, n_D^{20} 1.4805, m. p. 30°. The 1-ethynyl-1-cyclohexanol acetate was obtained, as described earlier [16], by acetylating the alcohol with acetic anhydride and had the constants: b. p. 66-67° at 3 mm, n_D^{20} 1.4670. 1-Vinyl-1-cyclohexanol was obtained by the partial hydrogenation of the acetylene alcohol (I) with Pd-catalyst and had the following constants [17]: b. p. 59° at 9 mm, n_D^{20} 1.4781.

Peracetic acid was obtained in known manner [18] by reacting acetic anhydride with 80-90% hydrogen peroxide.

Oxidation of 1-vinyl-1-cyclohexanol (II) with peracetic acid. Preparation of glycidol (III). To a solution of 25 g of 1-vinyl-1-cyclohexanol (II) in 200 ml of chloroform was added in 20 minutes by drops 20 g of 90% peracetic acid. The temperature of the reaction mixture was maintained at not above 25° by cooling the flask with cold water. The reaction mixture, showing stratification into two layers, was let stand at 20° for a day. The solvent was evaporated in vacuo, the residue, about 35 g, was dissolved in ether, washed with sodium bicarbonate solution, then with water, and dried over anhydrous sodium sulfate. Vacuum distillation gave 22.5 g (80%) of glycidol (III) as a colorless mobile liquid with b. p. 92.5-93° at 12 mm, n_D^{20} 1.4789, d_4^{20} 1.0585, MR 38.03; calc. 38.61 (the oxide ring increment was taken as equal to 0.7).

Found %: C 67.55, 67.63; H 9.92, 10.12. $C_8H_{14}O_2$. Calculated %: C 67.60; H 9.89.

Hydrolysis of glycidol (III). Preparation of triol (IV). A mixture of 2 g of glycidol (III), 100 ml of water and 5 ml of acetic acid was heated for 3 hours (at the boil). After filtering the solution and vacuum evaporation we obtained 2.1 g of triol (IV) as colorless needles with m. p. 114-114.5° (from ether) [19].

Found %: C 60.01, 59.93; H 10.21, 10.18. $C_8H_{16}O_3$. Calculated %: C 60.0; H 10.0.

Acidolysis of glycidol (III). Preparation of monoacetate (V). A solution of 25 g of glycidol (III) in 175 ml of glacial acetic acid was heated at 70-80° for 10 hours. The acetic acid was vacuum distilled, and the residue was also vacuum distilled. Here we obtained 25 g of monoacetate (V) as a viscous colorless sirup with b. p. 137-139° at 2 mm, n_D^{20} 1.4870.

Found %: C 59.60, 59.35; H 9.11, 9.19. $C_{10}H_{18}O_4$. Calculated %: C 59.41; H 8.96.

Preparation of diacetate (VII). To a solution of 15 g of acetic anhydride in 55 ml of pyridine was added under cooling 10 g of triol (IV) (m. p. 112-113°). Within 10 minutes all of the product went into solution. The temperature of the reaction mass was maintained at not above +20°. The solution was let stand for a day at room temperature, after which the reaction mass was poured into cold water and acidified with hydrochloric acid (62 ml). The product was extracted with ether, dried over sodium sulfate, and vacuum distilled. We obtained 12 g of diacetate (VII) as a viscous colorless sirup with b. p. 130-131° at 1 mm, n_D^{18} 1.4670.

Found %: C 59.09, 58.97; H 8.33, 8.08. $C_{12}H_{20}O_5$. Calculated %: C 59.02; H 8.19.

Preparation of triacetate (VIII). a) A mixture of 20 ml of acetic anhydride, 5 ml of dry pyridine and 3 g of triol (IV) was heated for 2 hours at 100-110°. The solution after cooling was poured into cold water, neutralized with aqueous sodium bicarbonate solution, the reaction product extracted with ether, and dried over anhydrous sodium sulfate. Vacuum distillation gave 3 g of triacetate (VIII) as a viscous colorless sirup with b. p. 130-131° at 2 mm, n_D^{20} 1.4620.

Found %: C 58.82, 58.68; H 7.78, 7.76. $C_{14}H_{22}O_6$. Calculated %: C 58.74; H 7.69.

b) A solution of 11 g of glycidol (III) in 50 ml of acetic anhydride was boiled in the presence of 0.1 g of potassium acetate for 4 hours. The acetic anhydride was vacuum distilled, the residue diluted with water, and then neutralized with sodium bicarbonate solution. The product was extracted with ether, dried over sodium sulfate, and vacuum distilled: 1st fraction, b. p. 102-125° at 2 mm, n_D^{20} 1.4635 (4.3 g); 2nd fraction, b. p. 125-130° at 2 mm, n_D^{20} 1.4615 (5 g); 3rd fraction, b. p. 130-132° at 2 mm, n_D^{20} 1.4600 (8.2 g).

The 3rd fraction was the triacetate (VIII). A small amount of the glycidol acetate (IX) was isolated from the 1st fraction as a colorless mobile liquid with b. p. 96.5-98.5° at 2 mm, n_D^{20} 1.4650, d_4^{20} 1.0762, MR 47.27; calc. 47.98 (the oxide ring increment was taken as equal to 0.7).

Oxidation of vinylcyclohexanol acetate (IIa) with peracetic acid. Preparation of acetate (X). To a solution of 40 g of acetate (IIa) (b. p. 83° at 13 mm, n_D^{20} 1.4590) in 200 ml of chloroform was added in drops and under cooling with ice water 30 ml of 80% peracetic acid. Self-heating of the reaction mass was not observed. The solution was let stand at 20° for three days. Then the acetic acid and chloroform were vacuum distilled, and the residue was also vacuum distilled; here we obtained about 10 g of starting acetate (IIa) and 20 g of tertiary acetate (X) as a very viscous colorless sirup with b. p. 137.5-138° at 4 mm, n_D^{20} 1.4860.

Found %: C 59.22, 59.06; H 8.97, 8.99. $C_{10}H_{18}O_4$. Calculated %: C 59.41; H 8.96.

Oxidation of cyclohexylideneethanol (XI) with peracetic acid. Preparation of glycidol (XII). To a solution of 8 g of cyclohexylideneethanol (XI) (b. p. 96.5-97° at 12 mm, n_D^{17} 1.4970; obtained by the allyl isomerization of 1-vinyl-1-cyclohexanol in known manner [4]) in 50 ml of chloroform was added in drops 10 ml of 80% peracetic acid. The oxidation proceeded with heat evolution. The reaction mixture was let stand a day at room temperature (15°). After the usual treatment and vacuum distillation we obtained 5 g of glycidol (XII) as a colorless liquid with b. p. 102° at 3 mm, n_D^{20} 1.4790, d_4^{20} 1.0530, MR 38.24; calc. 38.61.

Found %: C 67.14, 67.27; H 9.89, 9.93. $C_8H_{14}O_2$. Calculated %: C 67.60; H 9.89.

Hydrolysis of glycidol (XII) gave the above described triol (IV).

Oxidation of cyclohexylideneethanol acetate (XIII) with peracetic acid. Preparation of glycidol acetate (XIV). To a solution of 12 g of acetate (XIII) (b. p. 93.5-94° at 8 mm, n_D^{20} 1.4735, d_4^{20} 0.9825), obtained by the allyl isomerization of either 1-vinyl-1-cyclohexanol (II) or its acetate (IIa) with trichloroacetic acid [4], in 75 ml of chloroform was added in drops 15 ml of 60% peracetic acid. The temperature of the reaction mixture was maintained at not above 20° by cooling the flask with cold water. To complete the reaction the mixture was let stand a day at room temperature. After the usual treatment and vacuum distillation we obtained 10 g of glycidol acetate (XIV) as colorless liquid with b. p. 83.5-84° at 2 mm, n_D^{20} 1.4672, d_4^{20} 1.0576, MR 48.29; calc. 47.98.

Found %: C 64.93, 65.17; H 9.03, 9.09. $C_{10}H_{16}O_3$. Calculated %: C 65.22; H 8.69.

Hydrolysis of glycidol acetate (XIV). Preparation of acetate (VI). From 8 g of glycidol (XIV) after hydrolysis with acidulated water (250 ml of water and 7 ml of glacial acetic acid), as described above, we obtained 7 g of primary acetate (VI) as a viscous colorless sirup with b. p. 140-143.5° at 3 mm, n_D^{20} 1.4840.

Found %: C 60.02, 60.23; H 9.24, 9.12. $C_{10}H_{18}O_4$. Calculated %: C 59.41; H 8.96.

Preparation of β-cyclohexylideneethyl chloride (XVII). Into a solution of 35 g of 1-vinyl-1-cyclohexanol (II) in 700 ml of dry ether under cold water cooling was passed dry hydrogen chloride gas to a weight increase of 15 g (the calculated amount is 10 g). After 1.5 hours the water layer was separated, the ether solution washed thrice with water, and dried over potash. Vacuum-distillation gave 8 g of β-cyclohexylideneethyl chloride (XVII) as a colorless liquid with b. p. 80° at 17 mm, n_D^{20} 1.4950 [20].

Oxidation of β-cyclohexylideneethyl bromide (XV) with peracetic acid. Preparation of bromo oxide (XVI). A solution of 21 g of β-cyclohexylideneethyl bromide (XV) (b. p. 67-70° at 3 mm, n_D^{20} 1.5220), obtained from 1-vinyl-1-cyclohexanol (II) by the earlier described method [6], in 100 ml of chloroform was treated with 16 ml of 80% peracetic acid. The temperature of the reaction mass was maintained at not above 20° by cooling the flask with cold water. The mixture was let stand for 2 days at room temperature, and after distilling off the acetic acid and chloroform the residue was vacuum distilled; here we obtained 20 g of the bromo oxide (XVI) as a colorless liquid with characteristic odor, b. p. 78-78.5° at 2 mm, n_D^{20} 1.5040, d_4^{20} 1.3564; MR 44.73; calc. 44.85.

Found %: C 46.96, 47.18; H 6.43, 6.67; Br 36.39, 36.56. $C_8H_{13}OBr$. Calculated %: C 47.34; H 6.34; Br 39.0.

Oxidation of β-cyclohexylideneethyl chloride (XVII) with peracetic acid. Preparation of chloro oxide (XVIII). To a solution of 8 g of β-cyclohexylideneethyl chloride (XVII) in 60 ml of chloroform was added in drops 15 g of 90% peracetic acid. The mixture was let stand two days at room temperature, the solvent was distilled off, and vacuum-distillation of the product gave 6 g of the chloro oxide (XVIII) as a colorless liquid with b. p. 68-68.5° at 2 mm, n_D^{20} 1.4789, d_4^{20} 1.0887, MR 41.78; calc. 41.95.

Found %: C 60.27, 60.33; H 8.29, 8.29; Cl 19.78, 20.07. $C_8H_{13}OCl$. Calculated %: C 59.83; H 8.10; Cl 22.09.

Acidolysis of chloro oxide (XVIII). Preparation of chlorohydrin (XIX). To a solution of 5 g of chloro oxide (XVIII) in 50 ml of glacial acetic acid was added 5 g of potassium acetate. Almost all of the potassium acetate dissolved. The solution was heated at the boil for 30 minutes, then diluted with 150 ml of water, extracted with ether, and the ether extracts dried over sodium sulfate. Vacuum-distillation gave two fractions: 1st fraction, b. p. 75-100° (2 mm), n_D^{18} 1.4968 (2.8 g); 2nd fraction, b. p. 110-115° (2 mm), n_D^{18} 1.4852 (1.0 g).

The 2nd fraction crystallized. After several recrystallizations from n-hexane the chlorohydrin (XIX) was obtained as silvery leaflets with m. p. 92.5-93°.

Found %: C 54.44, 54.47; H 7.83, 7.70; Cl 15.57, 15.56. $C_{10}H_{17}O_3Cl$. Calculated %: C 54.43; H 7.71; Cl 16.15.

Reaction of glycidol (III) with acetyl chloride. Preparation of chlorohydrin (XX). To the cooled complex, composed of 5.6 g of acetyl chloride and 70 ml of dry pyridine, was added 10 g of glycidol (III) in 10 ml of pyridine. Here self-heating was observed (for 20 minutes). After 2 hours the reaction mass was poured into 250 ml of cold water. The pyridine was neutralized with hydrochloric acid (under cooling), the solution was extracted with ether, and the ether extracts were washed with sodium bicarbonate solution and dried over sodium sulfate. The residue obtained after distilling off the ether crystallized when rubbed with isopentane for a long time. Recrystallization from isooctane gave 5 g of chlorohydrin (XX) as colorless plates with m. p. 53.5-54°.

Found %: C 54.19, 54.24; H 8.74, 8.92; Cl 19.57, 19.27. $C_{10}H_{17}O_3Cl$. Calculated %: C 54.43; H 7.71; Cl 16.15.

Addition of hypobromous acid to 1-vinyl-1-cyclohexanol acetate (IIa). Preparation of bromohydrin (XXI). To a solution of 70 g of acetamide in 150 ml of water, containing 50 g of ground calcium carbonate and cooled to −3°, was added dropwise in 2.5 hours under constant stirring and cooling 25 ml (78 g) of bromine. The reaction temperature was kept below 0°. The reaction mass was vacuum-filtered, and to the filtrate was added 60 g of sodium acetate, and then 60 ml of glacial acetic acid. To this buffered solution of hypobromous acid at +5° was added in 5 minutes 36 g of acetate (IIa); here a homogeneous solution was formed at first, and then after 2-3 minutes an emulsion appeared, and the temperature of the reaction mass simultaneously rose to +15°. The heat effect was observed for 10 minutes. A copious crystalline precipitate deposited when the temperature of the reaction mass began to fall, which was filtered and dried. Recrystallization from petroleum ether and n-hexane gave 50 g of bromohydrin (XXI) as silver-white leaflets with m. p. 95-96°.

Found %: C 45.47, 45.54; H 6.61, 6.49; Br 30.40, 30.45. $C_{10}H_{17}O_3Br$. Calculated %: C 45.30; H 6.42; Br 30.14.

Saponification of bromohydrin (XXI) with baryta water. A mixture of 10 g of bromohydrin (XXI) and 12 g of barium hydroxide in 140 ml of water was boiled under reflux for 2 hours. All of the bromohydrin went into solution. The solution was filtered, the filtrate evaporated in vacuo nearly to dryness, and the residue extracted with chloroform, and then with acetone. The chloroform solution gave about 0.1 g of triol (IV) crystals with m. p. 113-114° and 1.5 g of oil. The acetone solution gave 0.2 g of triol (IV) crystals and 3.5 g of oil. The oily products were combined and vacuum-distilled; here we obtained 3 g of glycidol (III), which was then hydrolyzed to the glycerol derivative (IV) with m. p. 113-114°.

Oxidation of bromohydrin (XXI). Preparation of bromoketol acetate (XXII). Ten grams of bromohydrin (XXI) with m. p. 95-96° was oxidized at 20° for a day with 15 g of chromic anhydride (4-fold excess) in 600 ml of glacial acetic acid. The main portion of the acetic acid was vacuum distilled at a bath temperature of 25°. The residue was neutralized with soda solution, extracted with ether, and the ether extracts dried over sodium sulfate. Vacuum distillation gave 6.4 g of bromoketol acetate (XXII) as a slightly colored liquid, darkening on standing. B. p. 126-127° at 3 mm, n_D^{23} 1.4970. The bromoketol (XXII) was immediately saponified with alcoholic potassium hydroxide solution.

Saponification of bromoketol acetate (XXII). Preparation of dihydroxyacetone (XXIII). To 5 g of the bromoketol (XXII) (b. p. 126-127° at 3 mm, n_D^{23} 1.4970) in 10 ml of methanol was added 15 ml of 10% methanolic potassium hydroxide solution. Here a precipitate of potassium bromide was obtained (about 1.5 g). The solution was acidified with acetic acid, evaporated in vacuo, and the residue extracted with ether. The ether extracts were dried over magnesium sulfate. Removal of the ether by distillation gave 3 g of viscous sirup, from which 0.5 g of the dihydroxy ketone (XXIII) was isolated as colorless crystals with m. p. 84-85.5° (from petroleum ether), its mixed melting point with the authentic specimen (m. p. 88-88.5°) was 85.5-87°. We also obtained 2.5 g of noncrystallizing liquid with b. p. 116-117° at 2 mm, n_D^{23} 1.4840, darkening on standing, and apparently being mainly the starting bromoketol (XXII).

Treatment of 1-vinyl-1-cyclohexanol with hypobromous acid. Preparation of dibromoethylcyclohexanol (XXV). a) To an aqueous solution of N-bromoacetamide (obtained in the usual manner from 70 g of acetamide and 40 ml of bromine) was added 40 ml of glacial acetic acid and 30 g of sodium acetate. To this solution was added under stirring 25 g of 1-vinyl-1-cyclohexanol (II). Immediately a brown-colored oil deposited, which was separated, dissolved in ether and dried over sodium sulfate. Removal of the ether by distillation gave 40 g of the dibromoethylcyclohexanol (XXV) as a nearly colorless viscous sirup, showing decomposition when vacuum distilled (n_D^{20} 1.5300).

b) To 12.8 g (0.1 mole) of the vinylcyclohexanol (II) in 100 ml of dry ether was added in drops, under stirring and at a temperature not exceeding 20°, 18 g of bromine (slight excess). After the usual treatment (neutralization with sodium bicarbonate and drying over sodium sulfate) we obtained about 27 g of the dibromocarbinol (XXV) as a viscous oil, distilling at 120-122° at 2 mm with partial decomposition.

Preparation of bromo oxide (XVI). A mixture of 28 g of the dibromocarbinol (XXV) and a solution of 90 g of barium hydroxide in 300 ml of water was stirred at 65-75° for 1.5 hours. The solution after cooling was filtered, and the filtrate was extracted with ether. The precipitate on the filter was also washed with ether. The ether extracts were dried over sodium sulfate and after distilling off the ether the residue was vacuum distilled; here we obtained 10 g of the above-described bromo oxide (XVI) with b. p. 77° at 2 mm, n_D^{20} 1.5010.

Addition of hypobromous acid to 1-acetoxy-1-ethynylcyclohexane (XXVII). Preparation of dibromoketol acetate (XXVIII). To an aqueous solution of N-bromoacetamide (obtained from 60 g of acetamide, 130 ml of water, 60 g of calcium carbonate and 78 g of bromine) was added 50 g of sodium acetate and

50 ml of glacial acetic acid. To this buffered solution of hypobromous acid was added in 5 minutes under stirring 29 g of the acetate (XXVII). The temperature of the reaction mass was kept below 20° by cooling with cold water. Soon a heavy oil separated, which rapidly crystallized. We obtained 58 g (95-97%) of the dibromoketol (XXVIII) as colorless crystals with m. p. 53-54° (from petroleum ether).

Found %: C 35.27, 35.16; H 4.13, 4.33; Br 46.52, 46.63. $C_{10}H_{14}O_3Br_2$. Calculated %: C 35.11; H 4.10; Br 46.75.

Debromination of dibromoketol acetate (XXVIII). To 20 g of zinc dust and 20 g of sodium acetate in 40 ml of glacial acetic acid was added under cooling and stirring 20 g of the dibromoketol (XXVIII). The reaction proceeded with strong self-heating. When self-heating had ceased the mixture was heated for 15 minutes to 80-85°. Then the acetic acid was neutralized with sodium bicarbonate solution, and the reaction product was extracted with ether, and dried over sodium sulfate. Vacuum-distillation gave 7.7 g (72%) of 1-acetoxy-1-acetylcyclohexane (XXIX) as a colorless liquid with b. p. 91° at 5 mm, n_D^{20} 1.4580.

The 2,4-dinitrophenylhydrazone melted at 155.5-156.5° (from alcohol) and failed to give a melting point depression with the authentic specimen, obtained by the hydration of the acetylene alcohol (I) and subsequent acetylation.

Found %: N 15.26, 15.44. $C_{16}H_{20}O_6N_4$. Calculated %: N 15.38.

Saponification of dibromoketol acetate (XXVIII). Preparation of β-pentamethyleneglyceric acid (XXX). A mixture of 50 g of the dibromoketol acetate (XXVIII) (not recrystallized), 90 g of barium hydroxide and 700 ml of water was stirred at 65° for 2 hours; here almost all of the dibromoketol went into solution. The solution was filtered, the filtrate evaporated in vacuo nearly to dryness, and the residue treated with 17% hydrochloric acid. Repeated extraction with ether gave 20 g (80%) of β-pentamethyleneglyceric acid (XXX) as colorless crystals with m. p. 117-118° (from ether) [13].

Found %: C 55.48, 55.38; H 8.13, 8.22. $C_8H_{14}O_4$. Calculated %: C 55.17; H 8.04.

Ethyl β-pentamethyleneglycerate (XXXVII). Two grams of the dihydroxy acid (XXX) was dissolved in 25 ml of anhydrous alcohol, containing 0.5 g of dry hydrogen chloride, and the solution was let stand for 1 hour at 20°, and then boiled for 6 hours under reflux. The ethanol was vacuum-distilled, and the residue was dissolved in ether, washed with aqueous sodium bicarbonate solution, and dried over sodium sulfate. Removal of the ether by distillation and recrystallization of the residue from petroleum ether gave 1.5 g of ethyl β-pentamethyleneglycerate (XXXVII) as colorless crystals with m. p. 44-45°.

Found %: C 59.60, 59.58; H 8.98, 9.02. $C_{10}H_{18}O_4$. Calculated %: C 59.41; H 8.91.

β-Pentamethyleneglyceric acid acetonate (XXXVIII). One gram of the dihydroxy acid (XXX) was dissolved in 25 ml of acetone, containing 1% of dry hydrogen chloride, and 7 g of anhydrous sodium sulfate was added. The mixture was let stand for 10 days at room temperature, then filtered, the filtrate evaporated in vacuo to dryness, and the residue recrystallized from isooctane. We obtained 0.5 g of β-pentamethyleneglyceric acid acetonate (XXXVIII) with m. p. 94-95° (the melt hardens and then melts a second time at 98-98.5°).

Found %: C 61.94, 61.87; H 8.45, 8.36. $C_{11}H_{18}O_4$. Calculated %: C 61.68; H 8.41.

β-Pentamethyleneglyceric acid diacetate (XXXIX). To 1 g of the dihydroxy acid (XXX) in 25 ml of ether was added 4 g of acetyl chloride (4-fold excess) and the resulting solution was boiled under reflux for 3 hours, using a calcium chloride tube to protect it from moisture. The ether and excess acetyl chloride were vacuum-distilled, and the residue of about 1.2 g crystallized. Two recrystallizations from ether gave the β-pentamethyleneglyceric acid diacetate (XXXIX) as silver-white needles with m. p. 97-98°.

Found %: C 52.30, 52.14; H 8.08, 8.13. $C_{12}H_{18}O_6 + H_2O$. Calculated %: C 52.17; H 7.2.

Addition of hypobromous acid to 1-ethynyl-1-cyclohexanol (I). Preparation of 1-dibromovinyl-1-cyclohexanol (XL). To a solution of N-bromoacetamide, prepared from 40 g of acetamide, 40 g of calcium carbonate, 100 ml of water, 66 g of bromine, 30 g of sodium acetate and 30 ml of glacial acetic acid, was added in drops, under stirring and cooling, 20 g of the acetylene carbinol (I). After several minutes the 43 g of deposited heavy oil was separated, dissolved in ether, neutralized with sodium bicarbonate solution, and dried over sodium sulfate. Vacuum distillation gave the 1-dibromovinyl-1-cyclohexanol (XL) as a viscous colorless liquid with b. p. 124-124.5° at 6 mm, n_D^{20} 1.5687, d_4^{20} 1.7504, MR 53.14; calc. 53.53.

Found %: C 34.11, 34.00; H 4.47, 4.59; Br 56.42, 56.29. $C_8H_{12}OBr_2$. Calculated %: C 33.92; H 4.23; Br 56.30.

When seeded with the crystalline isomer the substance (XL) fails to crystallize.

Debromination of the liquid 1-dibromovinyl-1-cyclohexanol (XL). To a mixture of 20 g of zinc dust, 20 g of sodium acetate and 21 ml of glacial acetic acid was added 20 g of the liquid dibromovinylcyclohexanol (XL). When self-heating (80-90°) had ceased the mixture was heated for 20 minutes to 80°. The precipitate was filtered, the filtrate evaporated in vacuo, the residue diluted in water, and extracted with ether. The ether extracts were neutralized with sodium bicarbonate and dried over sodium sulfate. Vacuum distillation gave 7 g (80%) of 1-ethynyl-1-cyclohexanol (I) with b. p. 57° at 5 mm, n_D^{20} 1.4820. The alcohol crystallized after cooling and melted around 25°. The product gave the usual test for acetylenic hydrogen with ammoniacal silver nitrate solution.

Dehydration of 1-dibromovinyl-1-cyclohexanol (XL). A mixture of 20 g of the dibromovinylcyclohexanol (XL) and 10 g of anhydrous finely-divided potassium bisulfate was heated under a vacuum of 28 mm at a bath temperature of 130°. After removal of the water by cleavage (about 1 g) the diene began to distill as a light yellow mobile liquid with b. p. 92-94° at 4 mm, n_D^{20} 1.5725. The obtained diene failed to condense with maleic anhydride (115-120°, 5 hours).

Isomerization of the liquid 1-dibromovinyl-1-cyclohexanol (XL). A mixture of 40 g of the above described liquid 1-dibromovinyl-1-cyclohexanol (XL), 90 g of barium hydroxide and 300 ml of water was stirred for 2 hours at 80-90°. The reaction mass was filtered, the precipitate washed on the filter with ether, and the filtrate extracted with ether. The ether extracts were combined and dried over sodium sulfate. Removal of the ether by distillation gave 29 g of viscous sirup, which gradually crystallized. Recrystallization from petroleum ether, and then from n-heptane, gave the crystalline isomer of the 1-dibromovinyl-1-cyclohexanol (XL) as slender silvery needles with m. p. 72.5-73.0° (on a block).

Found %: C 33.82, 33.92; H 4.23, 4.35; Br 56.51, 56.55. $C_8H_{12}OBr_2$. Calculated %: C 33.82; H 4.23; Br 56.30.

The crystalline dibromovinylcyclohexanol (XL) with m. p. 72.5-73° was also obtained in 95% yield by brominating 1-ethynyl-1-cyclohexanol (I) in the usual manner with bromine in carbon tetrachloride solution. The mixture of the two specimens failed to show a melting point depression.

Debromination of the crystalline dibromovinylcyclohexanol (XL). A heat effect failed to be observed when we debrominated the crystalline dibromovinylcyclohexanol (XL) with zinc dust, as described above; here also the acetylene carbinol (I) was obtained in 70% yield.

Preparation of dibromoketol acetate (XLII). To a solution of N-bromoacetamide, prepared from 90 g of acetamide, 90 g of calcium carbonate, 200 ml of water and 175 g of bromine, was added 70 g of sodium acetate and 50 ml of glacial acetic acid. Then under constant stirring and cooling was added 73 g of the dimethylethynylcarbinol acetate (XLI) [19]. The resulting oil (156 g) was separated in a separatory funnel, dissolved in ether, washed with aqueous sodium bicarbonate solution, and dried over sodium sulfate. Vacuum distillation gave 130 g of the dibromoketol acetate (XLII) as a heavy yellow liquid with b. p. 105-106° at 9 mm, n_D^{20} 1.5088, d_4^{20} 1.7349; MR 51.86; calc. 51.40.

Found %: C 28.10, 28.12; H 3.43, 3.45; Br 52.95, 52.97. $C_7H_{10}O_3Br_2$. Calculated %: C 27.83; H 3.31; Br 52.95.

Ethyl β, β-dimethylglycerate (XLIV). To a filtered solution of 20 g of barium hydroxide in 400 ml of water was added in drops, under efficient stirring and cooling with cold water, 10 g of the dibromoketol acetate (XLII). The product went into solution quite rapidly. A slight heat effect was observed. The dibromoketol was added in a period of 20 minutes. After 1 hour the clear solution was extracted with ether, and the water layer was evaporated in vacuo to dryness. To the dry residue of salts was added 50 ml of absolute alcohol and 10 g of concentrated sulfuric acid, and the reaction flask, fitted with a reflux condenser, was heated on the water bath for 6 hours. Then the precipitate of barium sulfate was filtered, the filtrate neutralized with aqueous sodium bicarbonate solution, extracted with ether, and dried over sodium sulfate. After distilling off the ether the residue was vacuum distilled. We obtained 3 g of the ethyl β,β-dimethylglycerate (XLIV) as a viscous colorless liquid with b. p. 70-71° at 2 mm, n_D^{20} 1.4415, d_4^{20} 1.0922, MR 39.20; calc. 39.23.

Found %: C 52.50, 52.71; H 8.96, 8.94. $C_7H_{14}O_4$. Calculated %: C 51.85; H 8.64.

Preparation of ethyl dimethylglycerate diacetate (XLV). A mixture of 1.5 g of the ethyl dimethylglycerate (XLIV) and 20 ml of acetic anhydride was boiled for 2 hours. The reaction mass was cooled, poured into cold water and acetic acid, and neutralized with sodium bicarbonate. The reaction product was extracted with ether and dried over sodium sulfate. Vacuum distillation gave 1.[illegible] g of the ethyl dimethylglycerate diacetate (XLV) as a colorless liquid with b. p. 86-88° at 1 mm, n_D^{20} 1.4288, d_4^{20} 1.0864, MR 58.23; calc. for diacetate 57.96 (for monoacetate MR 51.13; calc. 51.01).

Found %: C 54.14, 54.35; H 7.48, 7.59. Diacetate $C_{11}H_{18}O_6$. Calculated %: C 53.66; H 7.32.

In another experiment the treatment of the barium salt of the β,β-dimethylglyceric acid, obtained from 20 g of the dibromoketol acetate (XLII), 75 ml of anhydrous isobutyl alcohol and 18 g of concentrated sulfuric acid, gave 6 g (30%) of the known [11] isobutyl β,β-dimethylglycerate (XXXII) as a viscous, nearly colorless liquid with b. p. 112-113° at 8 mm, n_D^{20} 1.4430, d_4^{20} 1.0354, MR 48.65; calc. 48.47.

Found %: C 56.64, 56.65; H 9.11, 9.17. $C_9H_{18}O_4$. Calculated %: C 56.84; H 9.47.

SUMMARY

A detailed study on the glycidic and bromohydrin methods of introducing the dihydroxyacetone and glycerol side chains was made on the example of cyclohexanone, and also on the dibromoketol method of building the dihydroxypropanecarboxylic acid side chain.

A number of new cyclohexane derivatives were described, showing interest in connection with the problem of synthesizing corticoidal hormones and their simpler analogs.

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STUDY OF β-SITOSTEROL

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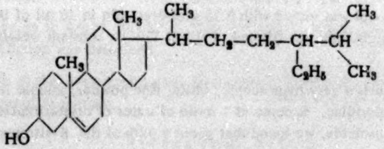
Earlier we had described methods for the isolation of β-sitosterol from crude phytosterol, and a study of the composition of the phytosterol isolated by the alkaline hydrolysis of pinewood [1]. It was found that the indicated crude contains up to 40% and more of β-sitosterol and differs from cholesterol only in the presence of a C_2H_5 group at the C_{24} side chain; as a result, β-sitosterol seems to be the C_{24}-ethyl derivative of cholesterol, having the structure:



In view of the fact that in the oxidation of cholesterol, as was shown by a number of authors [2], a side chain is eliminated with the formation of $\Delta^{5,6}$-dehydroepianhydrosterol-17, it seemed of interest to make a closer study of the properties of β-sitosterol.

First of all, it should be mentioned that the β-sitosterol is extremely labile and is easily changed under the influence of either temperature or ultraviolet illumination. In addition, similar to cholesterol, it always contains a certain amount of the dihydro derivative (dihydro-β-sitosterol) with m. p. 136-140.5° [3].

The acetylation of the dihydro-β-sitosterol gave us the 3-acetate with m. p. 134.5-135.5° (from the literature, m. p. 129-139° [4]). The acetylation of the β-sitosterol with acetic anhydride gave in good yields the β-sitosterol 3-acetate with m. p. 123-124° (from the literature, m. p. 120-121° [5]).

The bromination of the β-sitosterol 3-acetate with pyridine tetrabromide in dichloroethane medium proceeds very smoothly, and here we obtained an 89.3% yield of substance with m. p. 119-128°; the 5, 6-dibromo-β-sitosterol 3-acetate is stable at 20°, and decomposes at a higher temperature.

When our data are compared with the properties of the β-sitosterol and its dihydro derivative, isolated by foreign authors from either grain sprouts or soybeans, attention is attracted to the fact that the latter are identical and can be isolated in considerable amounts from the wastes of sulfite pulp production.

EXPERIMENTAL

Behavior of β-sitosterol toward ultraviolet and temperature. When exposed to ultraviolet illumination β-sitosterol shows either violet-blue or blue fluorescence. The lignoceryl alcohol ($C_{24}H_{49}OH$) of normal structure, usually accompanying β-sitosterol in crude phytosterol, shows bluish-gray fluorescence. The salts of lignoceric acid, also accompanying plant sterols, fail to fluoresce.

When β-sitosterol with m. p. 136.5-139.5° was heated in a thermostat to 105° for 4 hours a reduction in its melting point to 118-124° was observed; when heated to 120° for 3 hours its melting point dropped to 114-120°, and finally when heated to 120° for another hour the substance melted with the formation of a yellow waxy mass.

When β-sitosterol, previously illuminated with a quartz lamp at a distance of 15 cm, was heated a change in its melting point was observed (see table), i.e. at first the melting point showed sharp reduction, and then, after 12-18 hours, an increase, failing to reach the original level (i.e. the substance decomposes).

Time of illumination (in hours)	Melting point
1	131.5—135.5°
3	118 —125
7	99.5—108
10	97 —107
12.5	101 —110
15	107 —116
18	109 —118.5
20	120

Behavior of β-sitosterol toward digitonin. Similar to other sterols, in which the hydroxyl group at C_3 shows β-orientation, β-sitosterol is precipitated by digitonin. A solution of 0.04 g of β-sitosterol with m. p. 138-139° in 6 ml of 95% alcohol was mixed with 0.15 g of digitonin in 15 ml of 90% alcohol. The resulting precipitate of β-sitosterol digitonide was filtered, dried at 110° to constant weight, and weighed; found β-sitosterol 97.07, 97.08%. *

β-Sitosterol digitonide is a very hygroscopic, white, fine powder, soluble in acetone, ether, chloroform, benzene, ethyl acetate and pyridine. It contains 1 mole of water of crystallization. Although the digitonides of other sterols are usually insoluble, we found that about 0.02% of the β-sitosterol digitonide dissolves in 95% alcohol.

Dihydro-β-sitosterol. The presence of dihydro-β-sitosterol in β-sitosterol was determined in the following manner. A mixture of 14 g of β-sitosterol with m. p. 138-139° ($[\alpha]_D$ + 19°), 250 ml of chloroform and 62.5 g of acetic anhydride was gradually mixed under cooling with 62.5 g of concentrated sulfuric acid. After adding 10 ml of water and letting stand for 2 hours the upper green-colored chloroform layer was separated from the lower sulfuric acid layer, and to completely separate the β-sitosterol from its dihydro derivative the chloroform solution was again treated with acetic anhydride and concentrated sulfuric acid, washed several times with water, and to avoid emulsification, treated with 5 g of sodium chloride. The filtrate after distilling off the chloroform was mixed with 20 ml of 10% alcoholic potassium hydroxide solution (to saponify the β-sitosterol 3-acetate, arising in the acetic anhydride treatment), and after removing the alcohol (by distillation) and adding water, was extracted with ether. After filtration and ether removal, and also recrystallization from 75 ml of alcohol, in the presence of activated carbon, we obtained 0.6 g of substance with m. p. 139.5-140.5°, $[\alpha]_D$ + 23° (1% chloroform solution); from the literature, m. p. 136-140.5° [3]. Under the microscope (magnification 200 times) it was revealed that the substance crystallizes as plates, and differs from the crystal structure of β-sitosterol.

Dihydro-β-sitosterol fails to give the Liebermann-Burchard reaction (pink color with concentrated sulfuric acid and acetic anhydride), and under ultraviolet illumination shows a bluish-violet fluorescence.

β-Sitosterol 3-acetate. A mixture of 10 g of β-sitosterol, 5 g of acetic anhydride and 5 g of dichloroethane was heated under reflux at 95-98° for 5 hours. The crystals that separated on cooling were filtered and recrystallized from alcohol; we obtained 7.2 g (65.5%) of substance with m. p. 120.5-122°.

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* The composition of the digitonin E. Merck was $C_{59}H_{90}O_{29}$; 1 g of β-sitosterol digitonide dried at 110° corresponds to 0.2641 g of β-sitosterol.

The saponification of the β-sitosterol 3-acetate gave: found saponification number: 121.13, 121.90. $C_{30}H_{50}O_3$. Calculated saponification number: 121.55.

5,6-Dibromo-β-sitosterol 3-acetate. A mixture of 107.3 g of β-sitosterol with m. p. 135-137°, 54 g of acetic anhydride and 50 ml of dichloroethane was heated for 5 hours at 95-98°; then 200 ml of dichloroethane was added to dissolve the separated crystals, and then, under cooling to −14 to −15° and stirring, the pyridine tetrabromide, prepared from 46 g of bromine and 10.4 g of pyridine, was gradually added. After removing the dichloroethane by vacuum distillation at 45° and 30 mm the residue was extracted with 450 ml of methyl alcohol; cooling to 10° gave 144 g of substance with m. p. 117-124°. A second treatment of 42.47 g of technical product with dichloroethane and recrystallization from alcohol gave 38.11 g (89.3%) of 5,6-dibromo-β-sitosterol 3-acetate with m. p. 119-128°. (From the literature the substance melts around 128° [6]).

SUMMARY

1. The behavior of the β-sitosterol, isolated by the alkaline hydrolysis of pinewood, toward ultraviolet rays and heating was investigated; it was found that the β-sitosterol is heterogeneous (contains dihydro-β-sitosterol as impurity) and shows change when heated. Its melting point of 136.5-139.5° drops to 97° and then rises again to 120°.

2. The behavior of β-sitosterol toward digitonin was studied and the β-sitosterol digitonide was isolated (in nearly quantitative yield).

3. It was found that up to 4% of dihydro-β-sitosterol (m. p. 139.5-140.5°) is present in the β-sitosterol, and a method for its separation was described.

4. The acetylation of the β-sitosterol gave its 3-acetyl derivative, and subsequent bromination gave the 5,6-dibromo-β-sitosterol 3-acetate.

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[illegible]

The [illegible] Found [illegible]

Tables 3. Calculated [illegible]

2,5-Dibromo-[illegible]. A mixture of [illegible] of acetic anhydride and [illegible] was added to [illegible] the [illegible] tetrabromide, [illegible] removing the [illegible] of methyl alcohol [illegible] of technical product [illegible] dibromo-[illegible] acetate [illegible] [5]).

SUMMARY

1. The behavior of the [illegible]

2. The [illegible]

3. It was found that [illegible] and a method for its separation was [illegible]

4. The [illegible]

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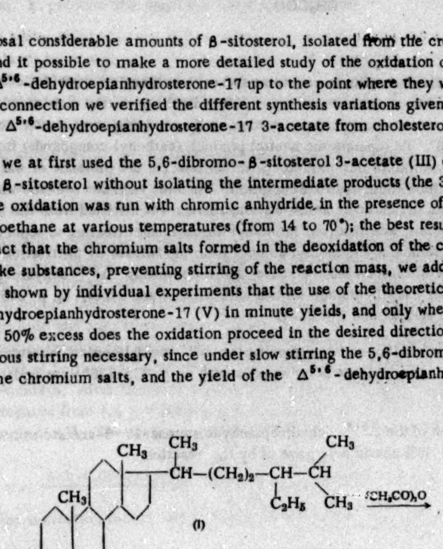
SYNTHESIS OF $\Delta^{5,6}$-DEHYDROEPIANHYDROSTERONE-17 FROM PINEWOOD STEROLS (β-SITOSTEROL)

A. M. Khaletsky and Li Chzhen-su

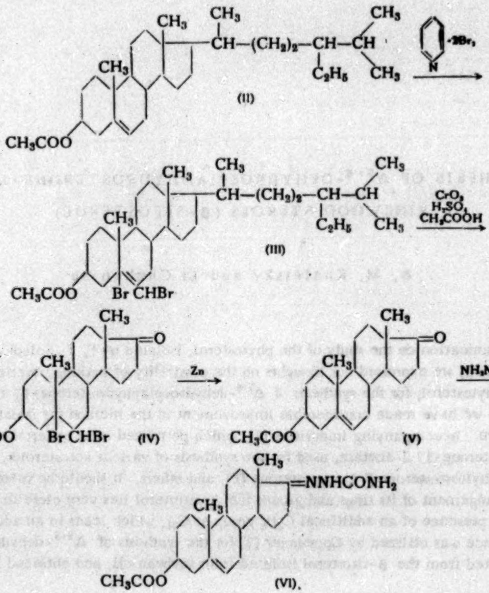
In our communication on the study of the phytosterol, isolated by F. T. Solodky [1] from the liquors of sulfite pulp production, we expressed our thoughts on the possibility of making practical use of the β-sitosterol, contained in this phytosterol, for the synthesis of $\Delta^{5,6}$-dehydroepianhydrosterone-17 and other steroids [2]. In the last seven years we have made considerable improvement in the method for isolation of the β-sitosterol and its purification from accompanying impurities [3], which permitted us to undertake the synthesis of $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate, used for the synthesis of various ketosteroids, and in particular, testosterone [4], 17-methyltestosterone [5], progesterone [6], and others. It should be mentioned that in its structure and the spatial arrangement of its rings and groups the β-sitosterol lies very close to cholesterol and differs from it only by the presence of an additional C_2H_5 group at C_{24}, which leads to an additional center of asymmetry. This substance was utilized by Oppenauer [7] for the synthesis of $\Delta^{5,6}$-dehydroepianhydrosterone-17; here the author started from the β-sitosterol isolated from soybean oil, and obtained low yields of the given steroid.

Having at our disposal considerable amounts of β-sitosterol, isolated from the crude phytosterol of sulfite pulp production, we found it possible to make a more detailed study of the oxidation of β-sitosterol and increase the yields of the $\Delta^{5,6}$-dehydroepianhydrosterone-17 up to the point where they were capable of competing with cholesterol. In this connection we verified the different synthesis variations given in the literature [8-12] for the preparation of the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate from cholesterol.

As starting product we at first used the 5,6-dibromo-β-sitosterol 3-acetate (III) obtained from β-sitosterol (I), and then we used the β-sitosterol without isolating the intermediate products (the 3-acetate or its 5,6-dibromo derivative). The oxidation was run with chromic anhydride in the presence of glacial acetic and sulfuric acids and dichloroethane at various temperatures (from 14 to 70°); the best results were obtained at 10-24°. In view of the fact that the chromium salts formed in the deoxidation of the chromic anhydride separated as thick, gel-like substances, preventing stirring of the reaction mass, we added either kieselguhr or sodium sulfate. It was shown by individual experiments that the use of the theoretical amount of oxidizing agent gives the $\Delta^{5,6}$-dehydroepianhydrosterone-17 (V) in minute yields, and only when the chromic anhydride is used in approximately 50% excess does the oxidation proceed in the desired direction. The heterogeneity of the system made vigorous stirring necessary, since under slow stirring the 5,6-dibromo-β-sitosterol 3-acetate deposited together with the chromium salts, and the yield of the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate dropped sharply.



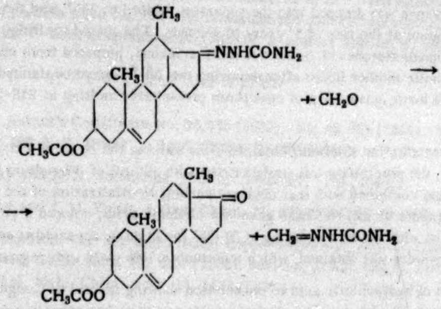
(I)



We used sodium bisulfite to deoxidize the excess chromic anhydride, after which the dichloroethane layer was separated from the aqueous layer. After distilling off the dichloroethane and acetic acid in vacuo at a temperature not exceeding 40° the residue, still containing some acetic acid, was debrominated with zinc dust at 20-23°. To separate the neutral products (carbonyl compounds) from the acid products (cholenic acids) the reaction mixture was extracted with benzene (in the presence of water), and the benzene solution was neutralized with sodium hydroxide solution. Then the benzene solution was treated with sodium hydroxide solution to separate the cholenic acids, and the solvent was distilled from the benzene solution. The residue, a viscous reddish mass, was dissolved in methyl alcohol under heating to separate the unreacted β-sitosterol 3-acetate. After removing the methyl alcohol from the filtrate by distillation the residue was treated with an alcoholic solution of semicarbazide acetate, and the resulting $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone (VI) was filtered and washed with alcohol and ether. M. p. 275° (with decomp.); from the literature, m. p. 274-276° and 279° [13].

From the mother liquor after removing the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone the semicarbazones of still some other ketones with m. p. 229-236° were isolated, which were not investigated further.

The reaction of the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone with formaldehyde in the presence of 80% acetic acid gave us by the reaction:



$\Delta^{5,6}$-dehydroepianhydrosterone 3-acetate in 89% yield. After purification with ether it melted at 168-169.5° (from the literature: m. p. 168-170° [14]).

EXPERIMENTAL

Oxidation of 5,6-dibromo-β-sitosterol 3-acetate. To 372.4 ml of glacial acetic acid and 92.9 g of chromic anhydride at 14-15° was gradually added under constant stirring 80 g of 5,6-dibromo-β-sitosterol 3-acetate (m. p. 119-128°) in 250 ml of dichloroethane, 92.5 g of sodium sulfate decahydrate and 22.4 ml of concentrated sulfuric acid (d 1.84). After 8 hours the reaction mixture was analyzed for the amount of unreacted chromic anhydride * and the excess of the latter was deoxidized with the theoretical amount of 34% sodium thiosulfate solution. In practice 100 ml of the latter was consumed.

After separating the water layer from the dichloroethane layer and washing the latter with water, and also extracting the water layer twice with dichloroethane (800 ml), the combined dichloroethane solutions were washed with water, neutralized with ~50 ml of 16.5% sodium hydroxide solution to Congo, and after separating the aqueous layer from the dichloroethane solution, the solvent was distilled off at 40° in vacuo. Any residual dichloroethane was removed by vacuum distillation at 20 mm.

Here there remained about 500 ml of reddish-orange liquid, which was subjected to debromination.

The debromination was run by adding to the oxidation product 40 g of zinc dust in individual portions at 20-23° in the course of 1 hour and subsequent stirring for 7 hours.

Separation of the oxidation products; isolation of the carbonyl compounds (as semicarbazones) and acids. To separate from excess zinc the reaction mixture was treated twice with 250 ml of benzene and 1200 ml of water, and after separating the benzene layer and washing the water layer (4.8 liters) with benzene, the latter was neutralized with 16.5% sodium hydroxide solution (150 ml), while the benzene solution was filtered through a 5 cm layer of sodium chloride and anhydrous sodium sulfate (1:1). Then the benzene was distilled from the filtrate at a temperature not exceeding 65° and a vacuum of 400-600 mm. The residue, a viscous brown-colored mass, was treated with 40 ml of boiling methanol under reflux, and then cooled to −3 to −5° to separate from unreacted β-sitosterol 3-acetate. After filtration and distilling off the methanol the residue was treated with semicarbazide solution, prepared from 4.4 g of semicarbazide hydrochloride and 6.4 g of sodium acetate in the presence of 55 ml of ethanol at 40°. The resulting precipitate was filtered, washed with 30 ml of hot alcohol, then 15 ml of ether, and dried at 50° to constant weight; we obtained 3.1-3.3 g of $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone with m. p. 297° (with decomp.). To determine the melting point, the capillary with substance was dropped into the apparatus, heated to 265°, and the determination was run by raising the temperature at the rate of 1° every 10 seconds. The mixed melting point with known authentic $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone, prepared from cholesterol, failed to be depressed. The alcoholic mother liquor after removing the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone, after 24 hours, gave 1.8 g of amorphous precipitate, melting at 218-230°, which was not subjected to closer study.

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* Using the calculation $x = \dfrac{a \cdot k \cdot 0.00333 \cdot 1000}{5}$, where a is the number of milliliters of 0.1 N sodium thiosulfate solution, k is the correction factor, and x is the amount of unreacted chromic anhydride.

The combined alkaline solutions, obtained after washing the benzene extracts, were allowed to settle and then decanted; the precipitate was washed twice with 125 ml of 3% sodium hydroxide solution, and the alkaline solution was combined with that obtained earlier. Neutralization of the given solution with 36% hydrochloric acid (about 25 ml) to Congo gave the cholenic acids, colored a yellowish brown, which after settling, decantation with water, and drying at 30-35° for 10 days, appeared as an amorphous brown powder; about 10 g of this powder was obtained, which represents a 19% yield with respect to the β-sitosterol.

The addition of hydrochloric acid to the solution showing neutral to Congo until it was acid (about 40 ml of 36% hydrochloric acid) also gave the cholenic acids as a tarry brown mass, which were decanted with water to negative reaction to Congo, and then dried at 40° for 10 days. We obtained about 24 g of acids as an amorphous brown powder, insoluble in water; the yield was about 40% with respect to the β-sitosterol. We give a table below, characterizing the yields of products in the oxidation of 5,6-dibromo-β-sitosterol 3-acetate and their melting points.

Amount of 5,6-dibromo-β-sitosterol 3-acetate taken on the basis of β-sitosterol in g	Filler	5,6-Dehydroepianhydrosterone-17, 3-acetate semicarbazone			Semicarbazones			Carboxylic acids				Total yield in %
								neutralized to Congo		isolated with hydrochloric acid		
		in g	in %	melting point	others in g	in %	melting point	in g	in %	in g	in %	
100.00	Kieselguhr	3.72	3.72	275°	1.66	1.66	238—246°	5.10	5.10	26.56	26.56	37.04
81.10	"	3.81	4.70	276	0.89	1.10	235—245	10.53	12.98	24.17	29.81	48.59
53.65	"	1.79	3.36	274	1.79	2.26	233—241	6.58	12.27	18.62	34.70	50.33
53.65	Sodium sulfate	2.74	5.11	279	0.33	0.62	223—231	6.67	12.43	18.22	33.96	62.12
53.65	the same	2.08	3.81	275	1.74	3.24	237—243	7.59	14.14	17.60	32.80	54.96
53.65	" "	3.30	6.11	279	0.96	1.79	218—230	8.15	15.84	14.48	27.00	50.49
53.65	" "	2.52	4.74	278	0.85	1.59	232—239	8.80	16.40	22.14	41.27	63.61
53.65	" "	3.14	5.86	279	1.48	2.76	212—221	6.43	11.96	18.86	35.16	55.76

$\Delta^{5,6}$-Dehydroepianhydrosterone-17 3-acetate. A mixture of 5 g of $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate semicarbazone with m. p. 279° (with decomp.), 3 ml of filtered formalin, containing 36% formaldehyde, and 30 ml of 80% acetic acid was heated for 2 hours on the water bath at 60-70°. The addition of 60 ml of water gave 4.03 g of substance with m. p. 161.5-166°. Recrystallization from ether gave 3.3 g of substance (89% with respect to the semicarbazone), m. p. 168-169.5°. Its mixed melting point with $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate, prepared from cholesterol, failed to be depressed.

SUMMARY

1. The oxidation of 5,6-dibromo-β-sitosterol 3-acetate with chromic anhydride in the presence of acetic and sulfuric acids, and also dichloroethane, was studied; here after debromination with zinc and removal of the solvent (dichloroethane) and acetic acid we isolated the neutral products as the semicarbazones, while the acid products were not studied closer.

2. From the semicarbazones we isolated the semicarbazone of $\Delta^{5,6}$-dehydroepianhydrosterone 3-acetate with m. p. 279°, which when reacted with formaldehyde under semicarbazide-exchange conditions was transformed into the $\Delta^{5,6}$-dehydroepianhydrosterone-17 3-acetate with m. p. 168-169.5°.

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[illegible] When the [illegible] we isolated the [illegible] of C^{14} [illegible] acetate with m. p. 57°, which when reacted with [illegible] exchange conditions was transformed into the C^{14}-diphenyl [illegible] with m. p. 190-191.5°.

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HIGH-MOLECULAR COMPOUNDS

XCVII. THE POLYMERIZATION AND COPOLYMERIZATION OF SOME SILICOOLEFINS

V. V. Korshak, A. D. Petrov, N. G. Matveeva, V. F. Mironov,
G. I. Nikitin and S. I. Sadykh-Zade

The synthesis and polycondensation of alkylsiloxanes have received quite detailed illumination in the literature. As regards the unsaturated silicohydrocarbons, considerably less attention has been devoted to them. At the present time a considerable number of unsaturated silicohydrocarbons has already been synthesized, however, their tendency to polymerize has still heen inadequately studied.

The first to study the problem of the polymerization of unsaturated silicohydrocarbons were S. N. Ushakov and A. M. Itenberg in 1937 [1]. They synthesized triethylvinylsilane and attempted its polymerization. However, as was found, this compound fails to polymerize when heated in the presence of benzoyl peroxide at 80 and 130° for 30 hours, and also when heated for 12 hours with 2-3% of strong sulfuric acid. K. A. Andrianov [2] obtained allyltriethoxysilane and showed [3] that the hydrolysis of this compound gives a polysiloxane with a molecular weight approximately 1.5 times greater than the calculated. He explained this divergence in molecular weights as being due to the fact that, together with the polycondensation process, there also proceeds polymerization. Yakovlev indicates that diallyldiethylsilane [4] is capable of polymerization in the presence of benzoyl peroxide and other catalysts. However, the properties of the polymer are not described. Allyltrimethylsilane [5] shows polymerization when treated with aluminum chloride. The substance formed here is a low-molecular product, with b. p. 290-340° at 15 mm, in which connection analysis of the polymer shows that, together with polymerization, some other processes are present. Hurd and Roedel [6] described the properties of polysiloxane polymers, possessing either the vinyl or allyl grouping, and also the ability of these polysiloxanes to copolymerize with styrene, dichlorostyrene, diethyl maleate, diallyl phthalate and butyl methacrylate, and described the properties of the obtained copolymers. Scott and Frisch [7] published on unsaturated chlorosilanes, which under hydrolysis and dehydration are transformed into polysiloxanes, capable of polymerization with the formation of reticular structures.

In the existing patent literature it is indicated that unsaturated silicohydrocarbons are capable of polymerization and of copolymerization with other monomers. Thus, for example, in [8] it is stated that the thermal polymerization of tetraallylsilane is accelerated in the presence of the alkali metals. Methallyltriethoxysilane, dimethallyldiethoxysilane, trimethallylethoxysilane, allyltriethoxysilane and diallyldiethoxysilane show copolymerization with maleic anhydride and the esters of maleic and fumaric acids [9] in the presence of benzoyl peroxide. Methallyltriethoxysilane copolymerizes with allyl phthalate [10] under the influence of tert-butyl perbenzoate. Such unsaturated silicoolefins as tetraallylsilane, triallylmethylsilane, tetravinylsilane and divinyldimethylsilane show copolymerization with styrene, methyl methacrylate or vinyl acetate to form reticular polymers [11]. Other statements of similar nature also exist [12-14].

For the purpose of studying the ability of unsaturated silicohydrocarbons to polymerize and to copolymerize with other monomers we investigated the tendency shown by the following silicohydrocarbons to polymerize and to copolymerize with methyl methacrylate and styrene: tri-n-butylallylsilane, methyldiallylsilane, dimethyldimethallylsilane, tetramethallylsilane and dimethylphenylvinylethynylsilane. The syntheses of the indicated compounds were described earlier [15-18], while their physical constants are given in Table 1.

Polymerization of the unsaturated silicohydrocarbons was effected by the method of heating them for 50 hours at 100 and 160°, both in the presence of benzoyl peroxide and in its absence, and also under the influence of aluminum chloride and boron trifluoride etherate at −60° in chloroform solution. However, as was found, tri-n-butylallylsilane, dimethyldimethallylsilane, tetramethallylsilane and methyldiallylsilane fail to form high-molecular compounds under the indicated conditions. Only dimethylphenylvinylethynylsilane shows polymerization when stored at room temperature to yield a trimeric clear gel-like polymer.

TABLE 1

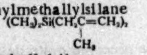
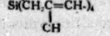
Expt. Nos.	Silicohydrocarbons	Boiling point	Pressure (in mm)	n_D^{20}	d_4^{20}	Literature reference
1	Tri-n-butylallylsilane $(n\text{-}C_4H_9)_3SiCH_2CH=CH_2$	135°	12	1.4534	0.8031	[15]
2	Methyldiallylsilane $CH_3HSi(CH_2CH=CH_2)_2$	122.5	745	1.4430	0.7630	[16]
3	Dimethylmethallylsilane  $(CH_3)_2Si(CH_2\underset{\substack{\vert\\CH_3}}{C}=CH_2)_2$	178—185	758	1.4515	0.8012	[17]
4	Tetramethallylsilane  $Si(CH_2\underset{\substack{\vert\\CH}}{C}=CH_2)_4$	269.5	745	1.4950	0.8609	[17]
5	Dimethylphenylvinylethynylsilane $(CH_3)_2C_6H_5SiC\equiv C-CH=CH_2$	83—84	65	1.5391	0.9229	[18]

TABLE 2

Copolymers of Silicohydrocarbons with Methyl Methacrylate

Silicohydrocarbons	Melting point of the copolymer	Solubility of copolymer in mixture of monomers	Yield of copolymer in %	Copolymer wt. (in g) dissolved in 10 ml benzene	Relative viscosity	Viscosity number	Analysis (in %) C	H	Si	Ratio of monomers in copolymer n/m*
Tri-n-butylallylsilane	190—205°	None	17.00	0.0746	0.446	59.78	61.58, 61.46	8.69, 8.46	Traces	—
Dimethyldimethallylsilane	170—185	None	19.41	0.0735	0.1575	21.43	60.26, 59.95	8.11, 8.17	to 1.5	17.026
Tetramethallylsilane	235—250 (decomp)	Soluble	100	Trimer			62.52, 62.60	8.58, 8.73	3.94, 4.26	4.364
Methyldiallylsilane	220—230 (decomp)	Soluble	12.43	0.0703	0.2906	41.05	65.67, 65.02	8.93, 9.11	6.92, 6.69	2.866
Dimethylphenylvinylethynylsilane	70—75	Soluble		0.0676	0.0739	10.93	72.45, 72.67	7.59, 7.55	13.00, 12.55	0.337

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* n is the number of methyl methacrylate radicals; m, silicohydrocarbon radicals.

Attempts to copolymerize the above-indicated silicohydrocarbons with methyl methacrylate and styrene proved more successful. The copolymerizations were run with a 1 : 1 molar ratio of the components at 100° for 50 hours in the presence of benzoyl peroxide. The copolymers were purified by pouring their benzene solutions into methanol to precipitate the copolymer. All of the copolymers precipitated as white powders, with the exception of the copolymers of dimethylphenylvinylethynylsilane and methyldiallylsilane with methyl methacrylate, which precipitated as viscous oils, becoming solid when the solvents were removed. The composition and properties of the obtained products are given in Tables 2 and 3. It is astonishing that only tetramethallylsilane forms a trimeric polymer with methyl methacrylate. Dimethyldimethallylsilane, the same as methyldiallylsilane, fails to form trimers. Tri-n-butylallylsilane fails to show a tendency to copolymerize with either styrene or methyl methacrylate, while methyldiallylsilane fails to copolymerize with styrene.

TABLE 3

Copolymers of Silicohydrocarbons with Styrene

Silicohydrocarbons	Melting point of the copolymer	Solubility of copolymer in mixture of monomers	Yield of copolymer (in %)	Wt. (in g) of copolymer dissolved in 10 ml benzene	Relative viscosity	Viscosity number	Analysis (in %)			Ratio of monomers in copolymer n/m*
							C	H	Si	
Tri-n-butylallylsilane	125—130°	Soluble	15.7	0.0634	0.1625	25.63	91.59, 91.58	8.28, 8.14	None	—
Dimethyldimethallylsilane	125—135	None	17.52	0.0625	0.0985	15.74	91.32, 91.05	8.04, 8.09	To 1.0	25.36
Tetramethallylsilane	130—140	Soluble	15.25	0.1007	0.6207	61.63	90.06, 89.91	8.74, 8.53	1.24. 1.54	18.9
Methyldiallylsilane	120—130	Soluble	25.39	0.0650	0.133	20.46	91.38, 91.10	7.33, 7.44	traces	—

* n is the number of styrene radicals; m, silicohydrocarbon radicals.

The composition of the copolymers (methyl methacrylate or styrene)$_n$ –(silicoolefin)$_m$ was determined from the silicon content, which varies from 1 to 13%, and was calculated by the formula:

$$\%\,\mathrm{Si} = \frac{28.06 \cdot m}{nM_1 + mM_2}\,100, \text{ from which } \frac{n}{m} = \frac{\dfrac{2806}{\%\,\mathrm{Si}} - M_2}{M_1}$$

, where n is the number of monomer M_1 radicals in the copolymer, and m is the number of monomer M_2 radicals. The characteristics of the copolymers are given in Tables 2 and 3.

SUMMARY

1. The tendency shown by the following unsaturated silicohydrocarbons to polymerize and to copolymerize with styrene and methyl methacrylate was studied: tri-n-butylallylsilane, dimethyldimethallylsilane, tetramethallylsilane, methyldiallylsilane and dimethylphenylvinylethynylsilane.

2. It was established that tri-n-butylallylsilane, dimethyldimethallylsilane, tetramethallylsilane and methyldiallylsilane fail to form high-molecular compounds, either when heated in the presence or absence of benzoyl peroxide, or under the influence of ionic catalysts – aluminum chloride and boron trifluoride etherate.

3. Dimethylphenylvinylethynylsilane shows polymerization at room temperature with the formation of a trimeric gel-like polymer.

4. Dimethyldimethallylsilane and tetramethallylsilane form copolymers with methyl methacrylate and styrene.

5. Methyldiallylsilane copolymerizes with methyl methacrylate and fails to copolymerize with styrene.

6. Of all of the silicoolefins, containing two or more double bonds, only the tetramethallylsilane forms a trimeric polymer with methyl methacrylate.

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* T. p. = C. B. Translation pagination.

HIGH-MOLECULAR COMPOUNDS

XCVIII. DEPENDENCE OF THE PROPERTIES OF MIXED POLYAMIDES ON THE NUMBER OF HYDROGEN BONDS

V. V. Korshak and T. M. Frunze

The mixed polyamides, being copolymers obtained as the polycondensation result of mixing two salts of hexamethyleneidamine with various dicarboxylic acids or of a hexamethylenediamine salt with a dicarboxylic acid and an amino acid, change their melting points as a function of the ratio of the starting substances. We studied [1-3] the changes in melting point on the examples of the following binary systems:* AH–AzH, AH–AT, AH–AFm, AH–AFo, AH–AFp, AH–GlH, AH–Kl, AH–PmH, AH–PH, AH–Pk, AH–SH, AH–SFm, AH–Uk, AH–Ek, AH–YaH, AzH–GlH, AzH–Kl, AzH–Pk, AzH–PmH, AzH–SH, AzH–Uk, AzH–Ek, SH–GlH, SH–Kl, SH–PmH, SH–Pk, SH–Uk, SH–SFm, SH–Ek, Kl–Pk, Kl–Ek.

An interesting property of all of the binary systems studied by us is the fact that in the vast majority of cases they show a minimum, in the case of the salts of two dicarboxylic acids, belonging to the mixed polyamide that was derived from the mixture of starting substances with a 60 mole % content of the longer acid. In the case of systems, formed from the hexamethylenediamine salt with a dicarboxylic acid and an amino acid, the minimum belongs to the compositions that contain from 60 to 80 mole % of the amino acid. To illustrate this, the change in melting point as a function of composition is shown in the Figure (Curve c) for the system AH–SH. The presence of a minimum becomes fully understandable if we attempt to explain it as being due to variation in the amount of amide groups present in the chain of the mixed polyamide macromolecule.

We had shown earlier [4, 5] that a direct relationship exists between the melting points of polyamides from even-numbered dicarboxylic acids and the number of amide groups found in the macromolecule chain. This relationship is expressed by the equation: $y = 7x + 110$, where y is the melting point of the polyamide, and x is the amount of amide groups with respect to the methylene groups in percent. For the polyamides from odd-numbered dicarboxylic acids such a relationship between the amount of amide groups and the melting point fails to be observed, which is explained by the fact that for such polyamides not all of the amide groups are capable of hydrogen bonding with the amide groups of adjacent macromolecules. For this reason a part of the amide groups, at times quite a considerable portion, remains free and does not form hydrogen bonds. As a result of this the melting point of the resulting polyamides shows decrease in direct proportion to the number of amide groups that fail to be linked by hydrogen bonds [4-6].

On this basis it can be postulated that also for the case of mixed polyamides, where the reduction in melting point is considerably greater than should be expected, the fact that some portion of the amide groups proves incapable of forming hydrogen bonds with the amide groups of adjacent macromolecules can serve as explanation.

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* Legend: A–adipic, Az–azelaic, Gl–glutaric, P–suberic, Pk–aminopelargonic, Pm–pimelic, S–sebacic, Uk–aminoundecanoic, Ek–aminoenanthic and Ya–succinic acids; Kl–ε-caprolactam, H–hexamethylenediamine, T–2,4-tolylenediamine, Fm–m-phenylenediamine, Fo–o-phenylenediamine and Fp–p-phenylenediamine.

At first glance the reason for this phenomenon is not fully understandable. Actually, as can be seen from the table, the amount of amide groups in the chain of a mixed polyamide macromolecule changes in direct proportion to the change in the number of methylene groups contained in both of the starting components.

From this it follows that a melting point change, if it were determined only by the amount of amide groupings, should proceed as a straight line function, and then a minimum would fail to appear on the curves of the binary systems. The change in melting point and content of amide groups for the system AH–SH is shown in the figure, where a is the amount of amide groups calculated from the structural formula, and b is the melting point change of this system, calculated from the equation given above.

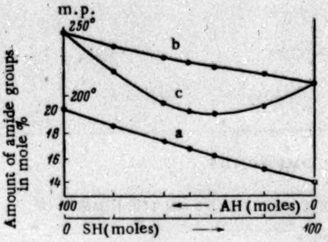


Figure 1

System AH–SH

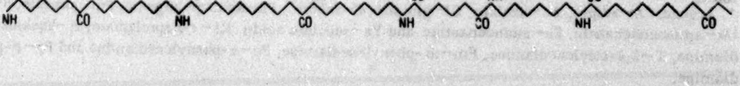
Ratio of starting substances AH/SH	Melting point	Amount (in mole %) of amide groups calculated from structural formula	Amount (in mole %) of hydrogen bonds, calculated from melting point	M. p. calculated from amount of amide groups	No. of amide groups linked by hydrogen bonds (in %)
1.0/0.0	250°	20.00	20.00	250°	100.00
0.8/0.2	220	18.52	15.72	240	84.83
0.6/0.4	190	17.24	11.43	230	66.29
0.5/0.5	190	16.66	11.43	226	68.60
0.4/0.6	185	16.13	10.71	223	66.39
0.2/0.8	190	15.15	11.43	216	75.44
0.0/1.0	210	14.28	14.28	210	100.00

Actually, the experimentally found melting points for the system AH–SH change along Curve c, which shows a well-defined minimum. This phenomenon can be explained by the fact that here, evidently, not all of the amide groups, found in the chain of the mixed polyamide macromolecule, prove capable of reacting with each other to form the hydrogen bond, and, as a result, a portion of the amide groups remains free, which leads to a reduction in the melting points of the copolymers, as can be seen from Curve c, shown in the figure.

Two reasons exist that render difficult the formation of hydrogen bonds between the amide groups of various macromolecules. The first reason is the fact that in the case of mixed polyamides a variable mutual distribution of the macromolecules is possible. Here in a number of cases the amide groups of different macromolecules prove to be in such juxaposition to each other that not all of them can react with the formation of a hydrogen bond, as is shown in the following schemes.

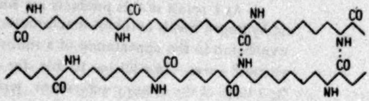
SCHEME 1

(100% of the amide groups are linked by hydrogen bonds)



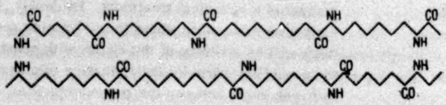
SCHEME 2

(50% of the amide groups are linked by hydrogen bonds)



SCHEME 3

(0% of the amide groups are linked by hydrogen bonds)



The presented schemes illustrate the case of the system AH−SH, where the ratio of starting substances is equal to 1 : 1; here we assume that the individual links of diverse nature show regular alternation, i.e., in the case of the system AH−SH the chain of the macromolecule will be constructed thus: . . . −A−H−S−H−−A−H−S−H− . . ., etc. The presence of regular alternation for diverse links is the result of the presence of polycondensation equilibrium. The latter includes in itself a number of exchange reactions, for the most part destructive in nature, and leads to exchange of links by diverse macromolecules [7]. As a result there occurs "averaging" of the composition of individual macromolecules, as had been shown by us earlier; here there also occurs "averaging" of the chain structure of the macromolecules, as had been shown by one of us on the example of the product obtained from sebacic acid and monoethanolamine [8]. This polyamide ester showed the following regular structure:

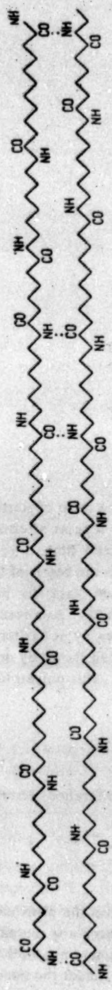
$$. . . -NH(CH_2)_2OOC(CH_2)_8CONH(CH_2)_2OCO(CH_2)_8CO- . . .$$

A study of the electronogram of this product indicated the absence of interference, corresponding to the nonregular structure:

$$. . . -NH(CH_2)_2OOC(CH_2)_8COO(CH_2)_2NHCO(CH_2)_8CO- . . .$$

On this basis it can be assumed that also for other polycondensation products the distribution of diverse links in macromolecular chains will be regular. Since in the equilibrium condition any mutual arrangements of the polyamide macromolecule are possible, then it is natural that the case where all 100% of the amide groups are linked by hydrogen bonds will be possible only under orientation, i.e. under the conditions of stretching the given specimen. In all remaining cases the number of hydrogen bonds between the macromolecules will change within the limits shown in the above schemes, which represent the limiting case for possible mutual arrangements of the macromolecules.

In the case of systems containing the starting substances in a different ratio, for example 2 : 3, the macromolecules are constructed in such manner that already in advance a uniform distribution of both components, forming the macromolecular links, is impossible, and consequently in the chain there appear accumulations of those links that were derived from the starting substances taken in excess. This creates even greater difficulties for regular distribution of macromolecules and leads to the situation that a still greater percent of amide groups proves incapable of forming hydrogen bonds, as was shown in the scheme for the system AH–SH, taken in the ratio 2 : 3.



SCHEME 4
(40% of the amide groups are linked by hydrogen bonds)

As a result of this products are formed, in which the least number of hydrogen bonds between macromolecules are present, which finds expression in the appearance of a minimum on the "composition–properties" curve. In addition to this, for copolymers obtained with a 2 : 3 ratio of the starting substances, less favorable conditions are created for macromolecular packing in the solid polymer, which also favors a melting point decrease. Incidentally, we will mention that in their structure the mixed polyamides that are obtained with an excess of one of the starting substances begin to approximate the vinyl type of copolymers, for which a nonregular link distribution in the macromolecular chain is characteristic [9]. The number of hydrogen bonds found in mixed polyamides should probably change as a function of the manner of mechanical treatment. Evidently, in the case of macromolecular orientation where the polyamide specimens are stretched there will be a sliding of the chains with respect to each other, and the possibility arises for the formation of a maximum number of hydrogen bonds between the macromolecules, which should find expression in a change in the mechanical properties of such polyamides.

SUMMARY

1. The question of the relationship between the melting points of mixed polyamides and the number of hydrogen bonds between macromolecules was examined.

2. An explanation was given for the presence of a minimum on the melting point – composition curve of mixed polyamides.

3. The question of the macromolecular structure of mixed polyamides was examined.

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THE REACTION OF KETENE WITH NITROGEN-CONTAINING BASES

II. ACETYLATION OF IMINO AND IMIDO GROUPS WITH KETENE

Yu. V. Svetkin

Based on the premise that ketene reacts with amines only in the presence of either H_2O or CH_3COOH, i.e. through acetic anhydride, we conducted some further studies in this direction. The present work again confirmed our earlier observations, and namely: diphenylamine, benzylaniline, phthalimide, 4-nitrophthalimide, succinimide, isatin, 4-nitroisatin and cytisine fail to react with ketene in absolutely anhydrous media. The acetylation of the above-enumerated imines and imides (with the exception of phthalimide, succinimide and isatin) proceeds smoothly only in the presence of either H_2O or CH_3COOH. All of these facts suggest that the acetylation initiator in the given reaction is apparently acetic anhydride.

The raised postulation is also supported by the observations of a number of authors [1-8], who in the ketene acetylation of optically active amino acids in aqueous alkaline solutions observed complete racemization of the reaction products at the moment when the pH of the reaction medium dropped below 7. Parallel experiments with acetic anhydride gave similar results [2-8]. The acetylation of $\underline{l}$(−)-cystine with ketene [9, 10] leads to the separation of free sulfur (similar results were obtained when $\underline{l}$(−)-cystine was reacted with acetic anhydride).

In the literature on the acetylation of alcohols and phenols with ketene many instances are cited where this reaction fails to lead to positive results in the absence of catalysts. Thus, Hurd and Roe [11] showed that phenols, tert-butyl alcohol and tert-isoamyl alcohol fail to be acetylated by ketene, while when traces of either H_2SO_4 or p-toluenesulfonic acid are added the results, in the words of the authors, are "striking" — the acetylation proceeds quantitatively. The same rules are also observed in the acetylation of cellulose with ketene [12]: the process proceeds smoothly only in the presence of $HClO_4$ or under preliminary treatment of the cellulose with glacial acetic acid.

Apparently, in all of the above-mentioned cases the acetylation proceeds through the mixed anhydrides of the corresponding acids. On the basis of general theoretical considerations we believe that the cleavage of a complex anhydride proceeds more easily, and consequently the acetylation proceeds more rapidly, the stronger the acid forming the anhydride. Such a behavior for ketene with alcohols gives a right to postulate the existence of an analogy in the reactions of ketene with an amino group and with a hydroxyl group. In all probability, the general conclusion is that ketene for all practical purposes fails to show direct reaction with either amines or hydroxyl-containing compounds in absolutely anhydrous media at normal temperatures. The exceptions in this respect are the lower members of the respective classes. On the basis of analyzing the above-outlined literature data, and also the results of our studies, it can apparently be considered an established fact that the acetylation of amines by ketene in the presence of either water or CH_3COOH is realized through the medium of acetic anhydride. This is all the more characteristic for those cases where the acetylation with ketene proceeds in aqueous media, since in the latter, as indicated by I. S. Ioffe [13], the acetylation of amines with acetic anhydride proceeds smoothly and vigorously without the influence of temperature and catalysts.

On the other hand, it is known that in the majority of cases the acetylation of amines with acetic anhydride in anhydrous media requires heat, catalysts, and a comparatively long reaction time.

The question arises: what is the reason for the higher chemical activity shown by the acetic anhydride that is obtained as the result of reacting ketene with either H_2O or acetic acid? We postulate that the ketene reacts with acetic acid, forming the enol form of acetic anhydride. At the moment that this form rearranges, the electron density distribution proceeds in such manner that the portion of the molecule in which hydrogen redistribution occurs, shows a greater electron attraction. This increased electron attraction determines the easy chemical reaction of acetic anhydride with amines.

Orientating statements with respect to the enolization of the reaction products of ketene with acids are found in the general literature [14, 15]. In the periodical literature only a number of studies, devoted to the given question, deserve consideration. Thus, in 1949 in paper [16], and also in a number of patents [17-19], mention is made of the reaction between hydrocyanic acid and ketene. The authors were unable to isolate the ketene cyanohydrin, but the fact of obtaining its acetate completely supports the formation of the enol in the reaction of ketene with the acid. The postulation was expressed by Illari [20] that the reaction of ketene with benzene in the presence of $AlCl_3$ proceeds via the enol mechanism.

Our experiments so far have not made it possible to isolate the enol form of acetic anhydride, but there is basis to assume that we will be able to show its presence in the near future.

Phthalimide, succinimide and isatin, both at normal and at elevated temperature, in anhydrous solutions and in aqueous acetone, ether, toluene, benzene and carbon tetrachloride, in either the absence or presence of CH_3COOH, CH_3COONa, CH_3COOK, H_2SO_4 or $ZnCl_2$, fail to be acetylated by ketene.

The introduction of a nitro group in the imide molecule activates the latter, as a result of which acetylation of the >NH group by our postulated method proceeds smoothly.

EXPERIMENTAL

Ketene was obtained by the pyrolysis of acetone at 740°.

Ketene fails to acetylate diphenylamine, benzylaniline, phthalimide, 4-nitrophthalimide, succinimide, isatin, 5-nitroisatin or cytisine in such absolutely anhydrous solvents as toluene, benzene, acetone, ether and carbon tetrachloride. The experiments were repeated many times, and in all cases we respectively took 50 g of substance and 80 ml of solvent. The acetone consumption was 250 ml in 1.5 hours. On conclusion of ketene passage the reaction mixture was distilled, where the starting substances and ketene polymers were always obtained in unchanged form and quantity.

Acetylation of diphenylamine in the presence of acetic acid. Five grams of diphenylamine with m. p. 52.9° was placed in a three-necked flask, fitted with a mechanical stirrer. The solvent taken was 80 ml of toluene, containing 3 ml of acetic acid. The ketene was bubbled through the reaction mixture under vigorous stirring. Within 10 minutes the temperature in the flask rose to 65° and remained there for 30 minutes; then in 15 minutes it dropped to 18°, after which the ketene addition was terminated. The acetone consumed for pyrolysis was 130 ml. The time of ketene passage was 55 minutes. The flask contents were transferred to a porcelain dish, half of the acetone was evaporated, and the residue on cooling deposited white crystals with m. p. 99°, and after recrystallization m. p. 102°, which corresponds to N-acetyldiphenylamine [21]. Saponification of the N-acetyldiphenylamine gave diphenylamine with m. p. 52°. The yield of the N-acetyldiphenylamine was 5.7 g (94%). In carbon tetrachloride, benzene and acetone solutions the yields varied from 80 to 90%.

Acetylation of benzylaniline in the presence of water. Five grams of benzylaniline in 80 ml of toluene, containing 0.5 g of water, was acetylated with ketene. The acetone consumption was 120 ml, and the time of ketene passage was 1 hour. The reaction temperature was 30-40°. Crystals with m. p. 58° were obtained, which corresponds to N-acetylbenzylaniline. Yield 5.4 g (93%). Saponification gave benzylaniline (m. p. 35°). Acetylation of the benzylaniline in the presence of acetic acid in acetone, ether, benzene and carbon tetrachloride solutions failed to show any essential advantages.

Acetylation of cytisine. A mixture of 3 g of cytisine with m. p. 153° and 60 ml of acetone, containing 0.2 ml of water, was placed in a three-necked flask. Here part of the cytisine failed to dissolve and remained as crystals. The ketene was entered into the reaction mixture under vigorous mechanical stirring. After 45 minutes, when the acetone consumed for pyrolysis reached 80 ml, all of the cytisine dissolved, and the ketone addition was terminated. The acetone was partially removed by distillation; the obtained substance had m. p. 192°, and after recrystallization 206-207°, which corresponds to N-acetylcytisine. Yield 3.2 g (92%).

Acetylation of 4-nitrophthalimide. A mixture of 4 g of 4-nitrophthalimide with m. p. 197° and 80 ml of toluene, containing 2 ml of glacial acetic acid, was placed in a three-necked flask. Part of the 4-nitrophthalimide remained undissolved; the ketene was added until the crystals disappeared completely. The solution assumed a yellow color; a part of the toluene was removed by distillation. The residue on cooling deposited crystals as needlelike stars, which were filtered and dried at 100°. Yield 94%. The obtained substance had m. p. 138.5°.

Found %: C 51.17, 51.24; H 2.51, 2.57; N 11.85, 12.10. $C_{10}H_6O_5N_2$. Calculated %: C 51.28; H 2.62; N 11.96.

Heating of the obtained substance to 250° resulted in decomposition with the liberation of free ketene, which with aniline gave acetanilide. From 4-nitrophthalimide and acetyl chloride in pyridine we obtained a crystalline substance with m. p. 138.5°. The mixed melting point with the substance obtained on the basis of using ketene failed to be depressed.

Acetylation of 5-nitroisatin. To 40 ml of toluene in a three-necked flask was added 2 g of 5-nitroisatin. To this reaction mixture was added 1 ml of glacial acetic acid. The acetone consumed for pyrolysis was 60 ml. Crystals with m. p. 193° were isolated as a reaction result, which corresponds to N-acetyl-5-nitroisatin [22]. Yield 82%.

SUMMARY

1. Ketene fails to react directly with imino and imido groups, and the acetylation of the latter proceeds only through acetic anhydride.

2. The nitro group activates imides, as a result of which the acetylation process proceeds smoothly.

3. The previously unknown N-acetyl-4-nitrophthalimide was obtained.

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SULFONIC ACIDS OF SULFONES AS SECONDARY PRODUCTS IN SULFONATION PROCESSES

I. FORMATION OF DIPHENYL SULFONE SULFONIC ACIDS IN THE SULFONATION OF BENZENE WITH OLEUM

A. P. Shestov

The conditions for the formation of sulfonic acids of sulfones in the sulfonation processes of aromatic compounds have been left almost completely unstudied [1].

In this communication we give the data of the studies made by us in 1945-1946 [2] on establishing the process for the formation of the sulfonic acids of diphenyl sulfone in the reaction of oleum with benzene under the conditions of obtaining m-benzenedisulfonic acid, and also on determining the necessary temperatures for complete conversion of benzenesulfonic acid to the m-disulfonic acid under the conditions of its sulfonation with excess oleum. This study direction was also of interest for the reason that contradictory opinions [3] exist as to the temperature (from 100 to 240°) necessary to form the m-benzenedisulfonic acid.

To solve the problems outlined above we took well-purified benzene and sulfonated it with 60% oleum containing a constant excess of SO_3. To avoid sulfuric anhydride losses by volatilization at elevated temperatures we ran the process in sealed ampuls. The sulfonation experiments were run at temperatures of 20, 50, 70, 90, 120, 160, 200, 220 and 240° and a constant reaction time of 3 hours.

The sulfonation mass was analyzed for the total amount of free SO_3 and H_2SO_4 (precipitation as $BaSO_4$), the total acidity, and the barium content in the barium salts of the sulfonic acids; in a number of experiments the sulfonic acids were converted into the corresponding sulfonyl chlorides, and the amount of the diphenyl sulfone disulfonyl dichloride in the mixture was determined by its poor solubility in ligroin. Later we used the polarographic method [4] to analyze the sulfonation mixtures.

From the analytical data we determined the degree of benzene sulfonation, i.e. the number of hydrogen atoms in the benzene ring that were substituted by the sulfuric acid radicals SO_3H and SO_2 (by the drop in total acidity during the sulfonation process), and also the number of hydrogen atoms in the benzene ring that were substituted by SO_3H groups (from a calculation of the acidity of the sulfonation mass based on the sulfo groups). The data, characterizing increase in the degree of sulfonation as a function of temperature, are shown in Fig. 1 and the table; they show in convincing manner the character of the reactions that proceed in the sulfonation of benzene with oleum and give an idea as to the order of the temperatures needed to transform the monosulfonic acid of benzene to the m-disulfonic acid. A comparison of

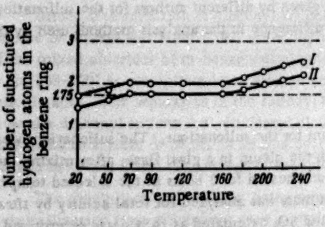

Figure 1. Relationship between the degree of benzene sulfonation by oleum and the temperature under the conditions of constant reaction time and SO_3 concentration.
I) Number of hydrogen atoms in the benzene ring substituted by SO_3H and SO_2 groups;
II) the same, but only SO_3H groups.

Curves I and II (Fig. 1) leads to the conclusion that the hydrogen atoms in the benzene ring are replaced by both SO_3H and SO_2 groups, i.e. sulfones are present, in the given case sulfonated sulfones, since the reaction products are completely soluble in water.

The amount of these sulfones remains constant from experiment to experiment and is of the order of 24-25%, based on charged benzene. The total number of hydrogen atoms, substituted in the benzene ring by SO_3H and SO_2 groups, remains equal to 2 in quite a considerable temperature interval (up to 160°), i.e., here we are dealing with a mixture of the disulfonic acids of benzene and diphenyl sulfone in amounts of approximately 75% m-benzenedisulfonic acid and 25% diphenyl sulfone 3,3'-disulfonic acid. This ratio is supported by the isolation of 25% (based on benzene) of the diphenyl sulfone 3,3'-disulfonyl dichloride from the reaction mixture.

Polarographic analysis of the reaction mixture obtained under the conditions of Expt. 4 (sulfonation at 90°) revealed on the polarographic curve the wave characteristic for diphenyl sulfone 3,3'-disulfonic acid, analogous to that described earlier [4]. The amount of diphenyl sulfone 3,3'-disulfonic acid, calculated from the taken polarograms, corresponds to 23.1%, based on sulfonated benzene.

Considering the accuracy of the methods used, the polarographic determination data showed good agreement with those presented earlier. The shape of Curve I in Fig. 1 shows that in the benzene ring the second hydrogen atom is substituted by a sulfuric acid radical (either SO_3H or SO_2) under treatment with oleum at comparatively low temperatures (at 70° for 3 hours), while at 180° there begins quite noticeable replacement of a third hydrogen atom (18% in 3 hours).

On the other hand, the presented experimental data, showing valid characterization of the process for the sulfonation of benzene by oleum, permit making certain postulations as to the reasons responsible for the contradictory representations made relative to the question of the temperature required for transformation of the monosulfonic acid of benzene to the m-disulfonic acid. Actually, if we exclude the observation made by us relative to the formation of sulfone sulfonic acids in the sulfonation of benzene, and consider our experimental data from a former viewpoint – the formation of only sulfonic acids of benzene – then the contradictory conclusions relative to the sulfonation temperature of the monosulfonic acid are superficially evident. Thus, if the degree of sulfonation is judged by the drop in acid titer, then the analyses show that the monosulfonic acid of benzene is converted to the m-disulfonic acid in 3 hours at 70° (Curve I, Fig. 1). If the degree of sulfonation is determined by the formation of sulfo groups, then the monosulfonic acid, as Curve II in Fig. 1 shows, is converted to the m-disulfonic acid in 3 hours only at about 220°.

Finally, if the degree of sulfonation is determined by the percent increase of barium in the barium salts of the sulfonic acid mixture, then the monosulfonic acid is converted to the m-disulfonic acid in 3 hours only at 240° (Expt. 10, table). On the surface this is a distinct contradiction.

The presented comparisons show that the temperatures given by different authors for the sulfonation of benzene to the m-disulfonic acid could be explained by the difference in the analysis methods used by them to determine the degree of sulfonation.

EXPERIMENTAL

We took purified benzene with f. p. 5.5° and c. p. oleum for the sulfonations. The sulfonations were run in two steps. In the first step the benzene was mixed with the oleum in a glass flask; after mixing the sulfonation mass was poured into ampuls, which were sealed and heated for 3 hours at the selected temperature. On conclusion of the established regime the sulfonation mass was analyzed for total acidity by titration with NaOH solution. The total amount of free sulfuric acid and SO_3 calculated as H_2SO_4 was determined by precipitation as $BaSO_4$. In a number of experiments a portion of the sulfonation mass was neutralized with barium carbonate. After removal from $BaSO_4$ the barium salts of the sulfonic acids were evaporated and dried at 180°, and the percent of barium in them was determined. In a portion of the experiments the mixture of sulfonic acids was converted in the usual manner into a mixture of sulfonyl chlorides, and the latter were separated by washing with ligroin. The polarographic method was used to analyze the sulfonation mass obtained by the regime of Expt. 4 (see table).

On the basis of the obtained analytical data we calculated: a) the total number of hydrogen atoms in the benzene ring substituted by sulfuric acid radicals (SO_3H and SO_2), based on the alkalimetric determination of the number of sulfuric acid equivalents consumed for sulfonation; b) the number of hydrogen atoms in the benzene ring substituted by SO_3H groups, calculated on the basis of determining the bound acidity, which depends on the sulfo groups; c) the percent barium content in the obtained mixtures of sulfonic acid barium salts; d) the amount of diphenyl sulfone 3,3'-disulfonic acid by the two methods indicated above.

The principal experimental data are given in the table below.

Sulfonation of Benzene with Oleum at Various Temperatures
(Duration 3 hours; common charge: oleum with 58.5% SO_3 662.2 g, benzene 156 g)

Expt. Nos.	Temperature	Acidity calculated as H_2SO_4* (in %)			Number of hydrogen atoms substituted by groups		Amount of barium in the barium salt** (in %)
		total	(free) $H_2SO_4+SO_3$	bound	SO_3H+SO_2	SO_3H	
1	20°	71.32	54.50	16.82	1.68	1.41	—
2	50	69.17	49.66	19.41	1.86	1.62	—
3	70	67.47	46.51	20.96	2.00	1.75	—
4	90	67.54	46.52	21.02	2.00	1.76	35.05
5	120	67.43	46.66	20.87	2.00	1.75	35.00
6	160	67.36	46.01	21.35	2.01	1.79	35.31
7	180	65.38	43.39	21.99	2.18	1.84	—
8	200	63.93	40.64	23.29	2.30	1.95	35.86
9	220	62.42	37.69	24.73	2.43	2.07	—
10	240	62.13	36.27	25.86	2.46	2.16	36.91

---

* Average of a number of determinations.

** The barium salt of the benzenedisulfonic acid contains 36.79% barium.

Determination of the barium content in barium salts. To establish the degree of accuracy of the method for determination of barium as $BaSO_4$ we ran a control determination in the medium of the used reagents on the amount of barium in pure $BaCl_2$. It was found that for 0.5 g of isolated $BaSO_4$ the deficiency from the calculated was 0.006 g.

Direct determination of diphenyl sulfone 3,8'-disulfonic acid. For the pure sulfonyl chlorides such a volume of solvent was taken (1000 ml of ligroin for 1 g of chlorides) as would permit obtaining in the separation of the mixed chlorides of m-benzenedisulfonic acid and diphenyl sulfone 3,3'-disulfonic acid the chloride with m. p. 168-170° as precipitate in an amount corresponding to the charged chloride of diphenyl sulfone 3,3'-disulfonic acid. The separation of the sulfonyl chlorides from the reaction mass of Expt. 4 (sulfonation at 90°) showed a diphenyl sulfone 3,3'-disulfonyl dichloride content of: 19.58, 19.43 and 19.39%, which respectively correspond to a yield of 24.38, 24.22 and 24.17% of diphenyl sulfone 3,3'-disulfonic acid, calculated on the basis of benzene, while the average of the three experiments is 24.26%.

The precipitate on the filter, being somewhat impure diphenyl sulfone 3,3'-disulfonyl dichloride, after recrystallization from chloroform gave a product with m. p. 180-180.6° (the literature m. p. is 175-176° [5]). Elementary analysis of the obtained sulfonyl chloride gave the following results:

Found %: C 35.15, 35.06; H 1.84, 1.96; Cl 16.51. $C_{12}H_8O_6Cl_2S_3$. Calculated %: C 34.7; H 1.94; Cl 17.08.

A mixture of this sulfonyl chloride with the sulfonyl chloride obtained from diphenyl sulfone failed to show a melting point depression.

From the diphenyl sulfone 3,3'-disulfonyl dichloride we prepared the corresponding sulfamide with m. p. 249.8° (the literature m. p. is 242° [5]).

Polarographic determination of diphenyl sulfone 3,3'-disulfonic acid. All of the polarographic determinations were run in the presence of 0.05 M tetraethylammonium iodide as the ground. The voltage was 3.8 V, the sensitivity 1/100, and the temperature 20°. On the polarograms shown the distance between the ordinates equals 0.2 V. The values of the half-wave potentials given below are always referred to a saturated calomel electrode.

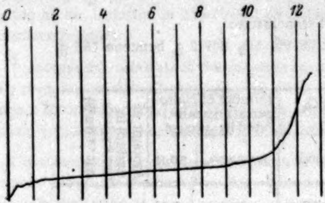

Figure 2

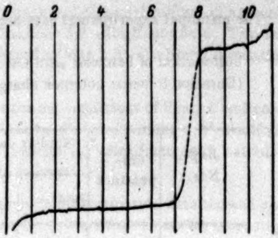

Figure 3

Polarographing of m-benzenedisulfonic acid. A 0.002 M solution of m-benzenedisulfonic acid was obtained by saponifying a known amount of the corresponding chloride with aqueous tetraethylammonium hydroxide solution. Its polarogram is shown in Fig. 2.

Polarographing of diphenyl sulfone 3,3'-disulfonic acid. A 0.002 M solution of diphenyl sulfone 3,3'-disulfonic acid was obtained by saponifying the pure chloride of the indicated acid with aqueous tetraethylammonium hydroxide solution. Its polarogram is shown in Fig. 3. From it are determined the wave height h = 69 mm, and the half-wave potential $\varphi_{1/2}$ = = −1.82 V.

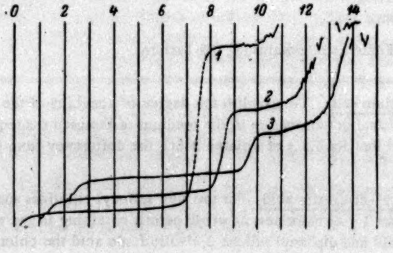

Figure 4

Polarographing of a mixture of diphenyl sulfone 3,3'-disulfonic acid and m-benzenedisulfonic acid. A solution was prepared by saponifying a mixture of the chlorides of diphenyl sulfone 3,3'-disulfonic acid and m-benzenedisulfonic acid, taken in a mole ratio of 1:3. Its polarogram is given in Fig. 4. From it the following wave height values were found: Curve 1) h = 71 mm, Curve 2) h = 35.5 mm, and Curve 3) h = 17 mm. The half-wave potential $\varphi_{1/2}$ ranges from −1.82 to −1.80 V.

The solutions show the following concentrations with respect to diphenyl sulfone 3,3'-disulfonic acid: Curve 1) 0.002 M, Curve 2) 0.001 M, and Curve 3) 0.005 M.

The curves shown in Fig. 4 were taken as being calibrated.

Polarographing of the sulfonation mass obtained under the conditions of Experiment 4. The sulfonation mass was neutralized with tetraethylammonium hydroxide, and from it a calculated 0.007823 M solution was prepared, based on the benzene taken for sulfonation. On the polarogram (Fig. 5) the wave height is measured to be h = 32 mm. Constructing a calibration curve on the basis of the polarograms in Fig. 4, we find the concentration of the diphenyl sulfone disulfonic acid to be 0.000901, which represents 23.1% on the basis of the benzene taken for sulfonation.

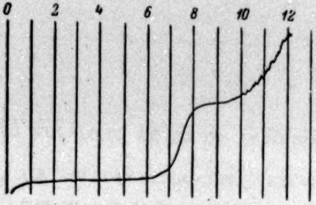

Figure 5

SUMMARY

1. In this study we established that the sulfonation of benzene with oleum gives, in addition to sulfonic acids of benzene, the sulfonic acids of diphenyl sulfone as secondary products. Complete conversion of the monosulfonic acids of benzene and diphenyl sulfone to the corresponding disulfonic acids begins at 70° in less than 3 hours with a slight excess of oleum.

Further noticeable entrance of sulfuric acid radicals (SO$_3$H and SO$_2$) into the benzene ring (due to substitution of a third hydrogen atom) begins at 160° and higher (with a reaction time of the order of several hours).

2. It was postulated that the presence of the fact that sulfonic acids of diphenyl sulfone are formed in the sulfonation of benzene with oleum could have led to the erroneous conclusions made in earlier investigations relative to the magnitude of the temperature (240°) needed to completely transform the monosulfonic acid of benzene to the disulfonic acid, since by the existing methods the sulfonic acids of diphenyl sulfone could have been determined as the monosulfonic acid of benzene.

3. It was established that by using 60% oleum in the sulfonation of benzene the amount of diphenyl sulfone disulfonic acid formed can reach 25%, based on charged benzene.

4. A more accurate understanding was given of the degree of sulfonation as determined by the number of hydrogen atoms substituted in the aromatic ring by sulfuric acid radicals (SO$_3$H and SO$_2$ groups).

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SULFONATION AND SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

XXVII. ALKYLSULFURIC ACIDS AS REAGENTS FOR THE CLEAVAGE OF RACEMIC COMPOUNDS *

A. P. Terentyev and V. M. Potapov

Investigators, desiring to use the third method of Pasteur for cleaving racemates of acidic nature, have the possibility of using numerous natural-occurring alkaloids as the asymmetric reagents. Considerably less choice is shown by acidic asymmetric reagents, suitable for cleaving racemic bases. Of the natural-occurring products only tartaric and malic acids show practical availability, and of the synthetic – compounds of the type of menthoxyacetic and camphorsulfonic acids. A limitation of all of the acidic asymmetric reagents known up to now is the fact that they are weak acids and consequently form quite unstable, easily hydrolyzed salts, especially with weak organic bases.

Having at our disposal a convenient and mild method for the conversion of alcohols to acid sulfates via reaction with dioxane sulfotrioxide [1], we set ourselves the task of utilizing the acid sulfates of optically active alcohols as asymmetric reagents for the cleavage of racemic amines. For this purpose we prepared the acid sulfates of (–)-borneol and (–)-menthol, with the aid of which we were able to cleave α-phenylethylamine and some of its analogs into the optical antipodes.

The acid sulfates of (–)-borneol and (–)-menthol proved to be very stable as salts in either neutral or alkaline medium (which has also been indicated by the few investigators who have worked with them earlier [2]). They withstand boiling with aqueous alkali for many hours. In acid medium they show gradual hydrolysis with regeneration of the starting terpene alcohol. Being strong acids, the sulfates of (–)-borneol and (–)-menthol with amines give salts that are practically resistant to hydrolysis, which permits running all of the operations in aqueous solutions, without having to resort to organic solvents.

In the literature several attempts are described to utilize the acid sulfates of alcohols for stereochemical purposes; however, here the problem solved was the reverse of ours: the racemic alcohols were converted into acid sulfates for the purpose of separating the alkaloid salts by crystallization. Thus, even Pasteur [3], and later Le Bel [4], separated the amylsulfuric acids, obtained from fusel oil, by the fractional crystallization of their cinchonine salts. Kruger [5] prepared the acid sulfate of ethylpropylcarbinol, probably also having stereochemical purposes in mind. However, apparently he was unable to effect its cleavage, and for this reason he only described the properties of the strychnine and morphine salts of this acid sulfate. Some success was achieved by Meth [6], who obtained a weakly active secondary butyl alcohol through the brucine salt of the acid sulfate. He was unable to effect cleavage of racemic amyl alcohol in a similar manner. Later a number of papers appeared on the cleavage of racemic glycols by their transformation into acid sulfates with subsequent crystallization of their alkaloid salts. This method was used to cleave propylene glycol [7], trans-cyclohexanediol [8], trans-1,2-cycloheptanediol [9], trans-1,2-cyclopentanediol and trans-1-methyl-3,4-cyclohexanediol [10]. Recently a patented method appeared on the cleavage of d,l-α-hydroxy-β,β-dimethyl-γ-butyrolactone (intermediate in the synthesis of pantothenic acid) via its reaction with chlorosulfonic acid to the corresponding acid sulfate and subsequent fractional crystallization of either the strychnine or brucine salt [11].

In practice two variants can be used to separate the racemates of amines through their salts with either (–)-bornyl- or (–)-menthylsulfuric acid. When operating with small quantities (of the order of hundredths of a mole) it is most expedient to mix hot aqueous solutions of the barium alkylsulfate and amine sulfate, remove the resulting barium sulfate precipitate by centrifuging, and separate the diastereomeric salts by several recrystallizations from hot water. When separating considerable amounts a different method is more convenient: the amine to be separated is added to the acid sulfate directly after the preparation of the latter (in dichloroethane solution). After some standing one of the diastereomeric salts formed here deposits from solution in quite pure condition and is purified further by recrystallization from water. The pure salt is decomposed with a slight excess of barium hydroxide and the optically pure amine is steam distilled. The second, more soluble diastereomeric salt was obtained as a noncrystallizing sirup when the solvent was removed by distillation, for which reason after precipitation and separation of the first precipitate we added water and barium hydroxide to the filtrate and steam distilled the second antipode (here it was obtained in a form not of complete optical purity). The asymmetric reagent was quantitatively regenerated as the barium salt.

EXPERIMENTAL

Barium salt of (–)-bornylsulfuric acid. To a solution of 23 ml of dioxane in 130 ml of dichloroethane under cooling and stirring was added a solution of 20.6 g of sulfur trioxide in 70 ml of dichloroethane,* and then 40 g of (–)-borneol ("pure" commercial product, $[\alpha]_D^{20}$ −35.2 in CH_3OH, p = 7.3, m. p. 202°) was introduced. Here the dioxane sulfotrioxide precipitate went into solution and the whole reaction mixture became liquid. After an hour the mixture was poured into water, neutralized with solid barium carbonate, and the dichloroethane and unreacted borneol (recovery 1.9 g) were removed by steam distillation. Evaporation of the water solution gave 61.6 g (79%) of the barium salt of (–)-bornylsulfuric acid as white scaly crystals, m. p. with decomposition 103-104° (from water), $[\alpha]_D^{20}$ −18.0° (water, p = 2.7).

Found %: Ba 20.85, 20.62. $(C_{10}H_{17}OSO_3)_2Ba \cdot 3H_2O$. Calculated %: Ba 20.88.

The barium salt of (–)-menthylsulfuric acid was obtained from (–)-menthol, having $[\alpha]_D^{22}$ −49°, in a manner completely similar to the preceding, with the yield being nearly quantitative, $[\alpha]_D^{18}$ −55.1° (water, p = 1.5), m. p. with decomp. 111-112°.

Found %: Ba 22.08, 22.12. $(C_{10}H_{19}OSO_3)_2Ba \cdot H_2O$. Calculated %: Ba 21.95.

Diastereomeric salts of α-phenylethylamine with (–)-bornylsulfuric acid. A solution of 5.1 g of α-phenylethylamine sulfate in 100 ml of water was mixed with a solution of 9.3 g of the barium salt of (–)-bornylsulfuric acid in 200 ml of water. The barium sulfate precipitate was separated by centrifuging and to extract any adsorbed salt was treated twice with 70 ml of hot water. Evaporation of the combined filtrates to a volume of 200 ml and cooling gave 3.43 g of deposit, the single recrystallization of which from water gave 2.7 g of the pure salt of d (+)-α-phenylethylamine** with (–)-bornylsulfuric acid, m. p. 163°, $[\alpha]_D^{18}$ −12.4° (water, p = 1.1); $[\alpha]_D^{18}$ −14.2° (CH_3OH, p = 1.9). Further recrystallization fails to change either the melting point or the optical rotation. Evaporation of the filtrate to 50 ml gave 3.62 g of deposit, from which a single recrystallization from hot water gave the salt of (–)-α-phenylethylamine with (–)-bornylsulfuric acid, m. p. 145°, $[\alpha]_D^{18}$ −18.9° (water, p = 1.3); $[\alpha]_D^{18}$ −20.8° (CH_3OH, p = 3.0).

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* With such an order of addition, the opposite of that recommended earlier [12], the mixture shows considerably less self-heating, and the time of addition is shortened. By cooling to 5-7° the dilute dichloroethane solutions of sulfur trioxide and dioxane can be mixed in a matter of a few minutes without noticeable self-heating, provided the flask is cooled with ice water.

** The relative configuration of α-phenylethylamine was established by Leithe [13], who combined (–)-phenylethylamine with l-alanine.

The difference in the crystalline form of the diastereomeric salts is so noticeable (the salt of the (+)-amine being prismatic needles, and that of the (-)-amine being cubic crystals) that here the crystals obtained by slow evaporation can be mechanically separated from each other.

Preparative cleavage of α-phenylethylamine. A solution of 22.1 g of sulfur trioxide in 100 ml of dichloroethane was added at 5-8° under mechanical stirring and cooling with an ice-salt mixture to a solution of 25 ml of dioxane in 50 ml of dichloroethane; then 44 g of (-)-borneol was introduced at 7-15°, and after this 34 g of α-phenylethylamine. Within several hours 44.9 g of precipitate separated, which after two recrystallizations from water gave 35.9 g of the pure salt of (+)-α-phenylethylamine with (–)-bornylsulfuric acid, m. p. 163°, $[\alpha]_D^{20}$ −17.3° (CH_3OH, p = 8). The solvent was removed from the dichloroethane filtrate by steam distillation (here 2.0 g of borneol also distilled); then an excess of barium hydroxide was added, and the distillation was continued. We obtained 12.4 g of (–)-α-phenylethylamine, $[\alpha]_D^{20}$ −24.9° (without solvent), i.e. the optical purity was about 63%.

To obtain the (+)-α-phenylethylamine the salt with $[\alpha]_D^{20}$ −17.3° was stirred with water and 1.1 equivalents of $Ba(OH)_2$; the amine was steam distilled and converted to the sulfate, which solution was evaporated, decomposed with alkali, the free amine extracted with either ether or benzene, dried, and distilled. In one of the experiments from 50.6 g of salt we obtained 20.2 g of (+)-α-phenylethylamine sulfate, $[\alpha]_D^{20}$ +5.70° (water, p = 2.1). From the sulfate we obtained 10.6 g of optically pure (+)-α-phenylethylamine, $[\alpha]_D^{20}$ + 40.6° (without solvent), b. p. 184-186°. From the low-boiling fractions and residue in the flask we isolated another 2.7 g of the (+)-amine as the sulfate.

Treatment with (–)-menthylsulfuric acid resulted in similar cleavage of: α-(m-xylyl)ethylamine: from the (–)-menthyl acid sulfate salt, having $[\alpha]_D^{20}$ −44.4° (CH_3OH, p = 3.2), we obtained the free (+)-amine, $[\alpha]_D^{20}$ + 25.5° (ether, p = 6); α-(p-xylyl)ethylamine: from the salt with (–)-menthylsulfuric acid, having $[\alpha]_D^{18}$ −46.9° (CH_3OH, p = 3.7) and m. p. 159°, we obtained the free (+)-amine, $[\alpha]_D^{18}$ + 32.0° (ether, p = 9).

Having failed to isolate the second antipode of these amines, and failing to find any data in the literature on their cleavage, we are not in a position to assert that the last two amines were obtained with complete optical purity.

SUMMARY

1. A new type of acid asymmetric reagents was proposed for the cleavage of racemic bases: the acid sulfates of optically active alcohols.

2. With the aid of the acid sulfates of (–)-borneol and (–)-menthol we were able to effect cleavage of α-phenylethylamine, α-(m-xylyl)ethylamine and α-(p-xylyl)ethylamine into their optical antipodes.

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LETTER TO THE EDITOR

An abstract (Abstractor M. Anderson) was published in Chemical Abstracts [49, 6761 (1955)], the contents of which differ somewhat from the contents of the paper on which it was based. We refer to the paper by M. I. Konarev and A. S. Solovkin "Reactions Between Zirconium Nitrate and the Iodates of the Alkali Metals in Solutions. III. The Influence of the Alkali Metals on the Composition of Zirconium Iodate and on Reactions in Which Precipitates are Formed", published in the Journal of General Chemistry [24, 1901 (1954)].

1. It is stated clearly in the paper that the $ZrOH^{+3}$-ion is formed in 0.07 N and more concentrated HNO_3 solutions, and not at pH 0.07 and more acid solutions, as given in the abstract.

2. The precipitates of the mono- and triiodate were isolated, and not the mono- and diiodate, as given in the abstract. The conditions under which the zirconium mono- and triiodate are formed are indicated in the paper.

3. It was shown in the paper that zirconium, in addition to the hydroxy compound, forms the hexa- and enaiodate, and not the heptaiodate, as indicated in the abstract. In general nothing is said in the paper about the heptaiodate.

4. In the paper it is stated that at high nitric acid concentrations the mother liquors contain, besides $Zr(IO_3)_4 \cdot 2KIO_3$, also $Zr(IO_3)_4 \cdot KIO_3 \cdot HIO_3$, while the abstract states that the main reaction product under the indicated conditions is the zirconium acid hexaiodate.

M. I. Konarev

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